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Fundamental concepts in chemical engineering*

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Summary—In the author's opinion, the "unit process" concept is completely against the logic of chemical engineering which pays no particular attention to the kind of atoms exchanged. Nevertheless, chemical changes cannot be left outside the field of that science.

In an attempt towards a general classification of all unit operations, some can be put together in accordance with their mechanical character. It is possible to classify all the others by the common character of exchange processes: momentum transfer, energy transfer, mass transfer, intramolecular transfer.

The proposed classification includes in the field of Chemical Engineering Science all the transformations carried out not only in the chemical industry but also in all the process industries.

Résumé—L'auteur se préoccupe de faire rentrer les transformations chimiques dans la systématique du GENIE CHIMIQUE, car il est peu satisfait du concept américain d'unit operation qui classe ces transformations suivant la nature des atomes échangés.

Il est conduit à proposer une systématique générale englobant toutes les opérations fondamentales. Après avoir séparé un certain nombre d'opérations à caractère purement mécanique, l'auteur est conduit à classer toutes les autres sous le nom générique de phénomènes d'échanges: échanges d'impulsion, échanges d'énergie, échanges de matière, échanges intramoléculaires.

Cette classification permet de faire rentrer sous la discipline du GENIE CHIMIQUE toutes les opérations intéressant non seulement l'industrie chimique, mais toutes les industries de transformation.

We think that everybody will now agree, that Chemical Engineering is a true science: it is one of the many branches of the physical sciences, exactly like electronics, physical chemistry or hydrodynamics. Chemical engineering has its own definite object: to conceive, to design, to build and to operate the equipment with which any kind of chemical reaction is to be performed on the industrial scale.

The idea of a true science of chemical engineering was certainly in the air before the end of the nineteenth century, in some papers of G. E. DAVIS from Manchester, as well as in those of G. LUNGE in Zürich or of H. LE CHATELIER in Paris. But I think that the first clear exposition

of the fundamental concept of chemical engineering was made by Dr. A. D. LITTLE in his Report to the President of the Massachusetts Institute of Technology in 1915:

"Any chemical process, on whatever scale conducted, may be resolved into a coordinate series of what may be termed 'Unit operations,' as pulverizing, drying, roasting, crystallizing, filtering, evaporating, electrolyzing, and so on. The number of these unit operations is not large and relatively few of them are involved in any particular process.

"The complexity of chemical engineering results from the variety of conditions as to temperature, pressure, etc. . . . under which

* This was delivered as a lecture to the University of London at University College, London, in January 1953.

the unit operations must be carried out in different processes and from the limitations as to materials of construction and design of apparatus imposed by the physical and chemical character of the reacting substances."

There we have clearly defined the fundamental concept of our science : one basic operation carried out in different circumstances varying from the manufacture of one product to the manufacture of others. Before this concept was fully understood, the craftsman was trained by hard experience to know all the "rules of thumb" to deal with, say, a sulphuric acid sludge in a lead chamber plant but he would be left helpless if asked to deal with the sweet liquor in a sugar refinery.

With the concept of unit operation, one has to understand that filtration is the kind of manipulation dealing with the mechanical separation through a porous medium of a fluid and the solid particles in suspension in it. Once the laws governing such a separation have been discovered and expressed mathematically in terms of general properties (density, viscosity, porosity, grist, etc. . . .), it suffices to give their special values in every particular case to all the numerical coefficients present in our mathematical relations. The design of a filter, adapted to any particular problem, will be possible through simple calculations.

As Dr. LITTLE said, the number of unit operations is not very large. It has not increased much since 1915. But we have to face something quite strange : a scientific discipline intended to control all the past and future developments of the chemical industry rests completely upon a scientific concept which leaves out all the changes which are purely chemical by nature. Is it not inconvenient that the chemical changes, which will remain the essential foundation of the chemical industry, are to be left outside the field of chemical engineering ?

A few of our American colleagues have tried to overcome that omission by the introduction of the additional concept of unit process. By unit process, they attempt to introduce the complete series of chemical changes like hydrogenation or reduction, oxydation, nitration, sulphonation,

halogenation and so on. Personally, I found it very difficult to make our students pass from the very clear-cut concept of unit operation to the new concept of unit process. By the unescapable diversity of practical conditions under which they are to be performed in industry, the chemical changes defy any attempt at classification. What is there in common really between the nitration of toluene to make trinitrotoluene with a mixture of sulphuric and nitric acid and the vapour phase nitration of paraffins with nitrous fumes ? Is there really something similar between the combustion of ammonia over a platinum catalyst and the cleavage of a double bond by aqueous permanganate, both chemical changes belonging to the oxidation unit process ?

In my opinion, it is useless to attempt to classify the chemical changes, by the nature of the atoms exchanged between different molecules ; I consider definitely that the concept of unit operation is completely against the logic of chemical engineering. Our science pays no particular attention to the kind of atoms exchanged ; it considers only the modalities of the chemical reactions.

Nevertheless, it remains essential to introduce the various chemical changes in the methodology of our discipline : chemical engineering cannot leave chemical reactions outside its field of interest.

Table 1.
Mechanical unit operations

| Size alteration | |
|---|-----------------------|
| Reduction | Enlargement |
| Crushing-Grinding | Pelleting-Briquetting |
| Disintegration-Pulverisation | Moulding-Sintering |
| Cutting-Machining | Extruding-Laminating |
| | Pressing-Flaking |
| Heterogenous Systems | |
| Separation | |
| Sampling-Screening | Kneading |
| Classification-Jigging- | Wetting-Dispersing |
| | Tabling |
| Sedimentation-Decantation | Atomisation |
| Elutriation-Filtration | Emulsification |
| Centrifugation-Expression | Homogenisation |
| Flotation | |
| Separation (magnetic or electrostatic) | |
| Dust and mist collection | |

In an attempt to overcome the difficulties of the unit process concept, I have tried to classify all the classical unit operations.

I shall immediately set apart a class of unit operations which are of a purely mechanical character (Table 1): some are utilised when we need to perform an alteration of form or of size: crushing, grinding, pulverizing, briquetting, sintering, laminating, extruding, etc. . . . We can also perform some other mechanical unit operations when, dealing with heterogeneous systems, we want to separate or to mix various phases: filtration, sedimentation, centrifugation, mixing, blending, atomizing, etc. . . .

For the remaining classical unit operations, like distillation, evaporation, crystallization, extraction, and so on, I think that their nature presents identical characters and I propose to class all of them under the French name "phénomènes d'échange" which I shall try to translate by "exchange operations" or by "transfer operations." It is necessary to note that in all these unit operations, our main interest lies in the kinetics of the transfer. Chemical engineering science is always obliged to investigate the migration of different molecular species through a surface of separation.

The introduction of the new concept of "transfer operations" appears purely as a matter of course when we stop considering chemical industry from the analytical side which made it possible to decompose any manufacture in series of unit operations. We must as well study the chemical industry in a synthetic way and try to find out what in it is always identical, no matter which products are considered.

Any chemical manufacturing process is primarily a problem of traffic. For the production of any kind of chemical, one of the first problems lies in the introduction of the raw materials and the removal of the final products. We have also to introduce into our equipment some form of energy: usually heat is wanted or must be extracted from our plants. Flow of fluids, heat transfer are major chapters of chemical engineering science. But it is obvious to me that here we have again some kind of physical "transfer operation."

For these two kinds of physical transfer operations, we are led to utilise mathematical relations of identical form: the relations of similitude will introduce the dimensionless numbers of REYNOLDS, of NUSSELT, of PRANDTL or GRASHOF. To explain convection phenomena, we are led to see a kind of barrier, or "transition layer" and we introduce the concept of the "film" discontinuity at the surface of separation: it is the same film which can be rendered visible by some experiments on the flow of fluids.

To interpret the diffusion of different kinds of molecules through the surface of separation between two phases, we will again utilize the properties of this special "film." It is perfectly logical to place together in the same chapter molecular transfer and momentum transfer or kinetic energy transfer: at the molecular scale, all these three exchange processes depend solely on individual contacts between real particles.

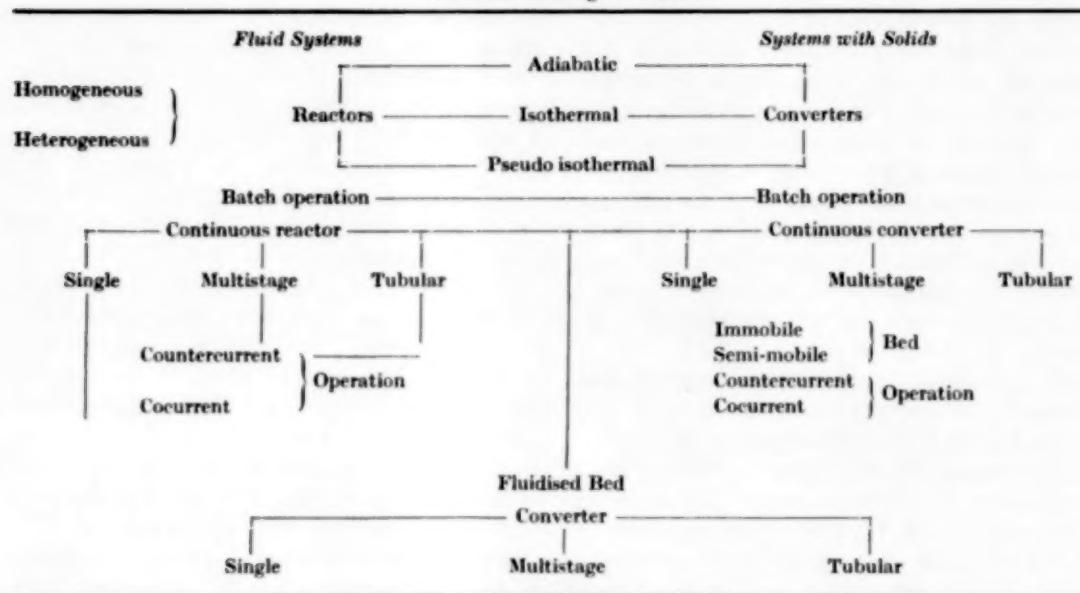
Finally, I can class together under the common heading of physical transfer processes three different kinds of physical transfer: momentum, energy, molecules (Table 2).

Table 2.
Physical Exchange Processes

| Momentum Transfer | Energy Transfer |
|---|---------------------------------|
| Flow of fluids (gases and ideal liquids) | Radiation Convection |
| Pumps-Fans-Compressors | Heat exchangers |
| Non-Newtonian Systems | Heat accumulators |
| Porous Beds-Suspensions | Thermophysics |
| Pneumatic transport | Heat engines |
| Hydraulic transport | Refrigerating engines |
| Mechanical handling | |
| <i>Mass Transfer</i> | |
| <i>Single Systems</i> | |
| Fusion-Solidification | Complex Systems |
| Sublimation | Distillation-Rectification |
| Vaporization | Solvent Extraction |
| Liquefaction | Dissolution-Crystallization |
| | Gases-absorption and washing |
| | Solids absorbents |
| | Drying |
| | Conditioning of gases |

But any chemical reaction is also an exchange process by which we interchange different atoms between different molecules. But chemical

Table 3.
Chemical Exchange Processes



engineering will pay no particular attention to the kind of atoms involved and remains interested only in the modalities of the transfer. As for all other transfer processes, chemical engineering will consider in the chemical changes, the driving force and the rate of exchange. All the chemical exchange processes will be classified according to the type of kinetics imposed by the circumstances under which they occur. These circumstances will vary from one reaction to the next but the nature of rate exchange will dictate the type of equipment required. Our classification of the chemical transfer processes will depend mainly on the different types of equipment : according to type of energy or mass transfer we are compelled to utilize different kinds of equipment.

For some particular chemical reactions, we want to prevent any heat exchange with the outside ; we need perfect thermal insulation : we will attempt an adiabatic operation. On the contrary, in some other cases, we need to maintain the temperature constant and we can achieve our isothermal transformation if we arrange to provide adequate heat transfer through the walls. Between these two extreme conditions of

operation, practical necessities will introduce intermediate imperfect modes of transformation : if the wall alone can be kept at constant temperature, we operate a pseudo-isothermal transformation.

About the mass transfer, the circumstances can also be extremely variable. In batch processes, we introduce in our equipment all the raw materials in the required sequence and after a certain delay we take away the final products. Chemical industry now utilises more and more continuous processes of manufacture. In the proper equipment, we feed at a steady rate the raw materials and obviously the character of our equipment will be dictated by the flow characteristics of our raw materials ; if we deal exclusively with fluids, the limitations of the equipment are less tight than if we have to deal with solids.

I consider that these differences in the flow characteristics of the raw materials, are so important for chemical engineering that I will introduce a more precise terminology. I shall give the generic name of "reactor" to the equipment dealing exclusively with fluids either homogeneous or heterogeneous. I shall reserve

the name of "converter" to the equipment dealing with mixtures of solids and fluids. Obviously converters and reactors can be run either batchwise or continuously. They can also be run either adiabatically or isothermally, or pseudo-isothermally.

For the continuous reactors, where we deal either with homogeneous or heterogeneous raw materials, we can consider first a type where they will stay long enough to give time for the chemical change to be achieved: we have a continuous single reactor. With a perfect stirrer, at every instant, we will find no variation of composition between different locations in our reactor.

In many cases, we may be obliged to fractionate our reactor in different compartments, each of them performing a definite step in the complete chemical transformation: we then deal with a compound reactor or multistage reactor. This equipment works in a completely different way to the single reactor: it makes easier the isothermal operation and it will be utilized if the chemical reaction requires different temperatures for the different steps. If the number of compartments or stages grows without limit, we arrive finally at the tubular reactor; in this type of equipment the fluids will flow at a constant rate and in every section we will reach a steady state of concentrations, velocities, temperatures, and so on.

With the multistage or tubular reactors, we can vary at will the local concentration of our reactants, as we can choose various feed points for our different raw materials. These feed points can be located at the opposite ends of our equipment and we will work counter-current wise, as opposed to cocurrent operation when all our initial reactants are fed at the same end and the final products withdrawn at the other.

If we deal with solid materials, we shall use converters which can be either adiabatic, isothermal or pseudo-isothermal. If our solid materials remain immobile, we have a fixed-bed converter: we can find many examples of fixed-bed converters in catalytic conversions. We can deal with single converters or with multistage converters in sulphur dioxide oxidation. In ammonia synthesis, we deal usually with tubular converters.

But in many other cases, the solid phase will play its part in the chemical change, but usually its movement is very slow compared with the flow of fluids. Our bed will be a semi-immobile bed: gas producers, blast-furnaces, rotary kilns or dryers are typical examples of our semi-immobile bed converters.

In scientific matters, some kind of classification is absolutely necessary to clarify our problems, but we must always remember that nature does not care for the limitations of our brains. Classification, always, must remain flexible. With the fluidisation we have the best example of the necessary transition step between the two extremes: reactors and converters. A fluidised bed equipment deals with solid particles and belongs legitimately to the converter class. But fluidized beds partake of the general properties of fluids and I cannot raise objections against fluidized bed converters being called also fluidized bed reactors.

It is not very long since chemical engineering has begun to investigate the characteristics of the different chemical exchange processes and to make the necessary distinctions between the different types of equipment best suited to different chemical reactions.

It gives me a real pleasure to pay a well deserved tribute to Dr. DENBIGH who was the first, I think, to give the lead in this new development of chemical engineering. In a paper published in the *Transactions of the Faraday Society* in 1944,* he put forward the theory of the continuous multistage reactor, a theory for the nitration process based on researches carried out during the war in the Royal Ordnance factories. DENBIGH extended very soon his theory to polymerization processes: the same type of theory deals adequately with changes involving very different kinds of chemical transformations.

In the United States, chemical engineers are now devoting their attention to the theory of converters, and we begin to learn how to design with some accuracy either adiabatic or isothermal or pseudo-isothermal converters.

* DENBIGH, K. G., *Trans. Faraday Soc.*, 1944, 40, 352-373; *Faraday Soc. Discuss.*, 1947, p. 263.

I really hope that my personal attempt at a close comparison between momentum or kinetic exchanges and molecular or atomic exchanges will not remain purely formal. The concept of a converter or a reactor especially adapted to a particular class of exchange is not really limited to purely chemical exchanges.

Let us look at the most usual equipment for mass exchanges between liquids and gases : the packed tower is usually employed for the physical absorption of soluble components, like ammonia or sulphur dioxyde in water. But it is also utilised when the absorption follows some chemical reaction as in the case of carbon dioxide and caustic solutions. What could tell the differences between a packed tower and a continuous tubular reactor ?

The bubble-cap plate tower is not basically different from DENBIGH's multistage reactor, except as to the efficiency of the mixing between

vapour and liquid. Perhaps this will open a new way of attack to a very old problem, still unresolved. In distillation, we know with a gratifying accuracy the equilibrium relationships between liquid and vapour compositions but we know very little about the rate of approach towards the equilibrium in our rectifying columns, in spite of what we can hear or read about theoretical plates, height equivalent to theoretical plates, height of transfer unit, Murphree efficiencies or over all efficiencies.

Perhaps, once the real identity between plate towers and multistage reactors has been accepted, it will be easier to find some way out of our present difficulties on the kinetics of distillation problems. Perhaps the applications of DENBIGH's line of attack about by-passing losses might give a quantitative account of the departure from equilibrium between liquid and vapour when we mix them on the plates of our stills.

On a problem of diffusion and simultaneous gas flow

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Summary—A diffusion problem of spherical symmetry, involving gas flow, has been treated quantitatively.

Résumé—L'auteur propose une solution quantitative pour un problème particulier de diffusion à symétrie sphérique, accompagnée d'un écoulement gazeux.

The following calculations were suggested by a paper presented by W. MORAWIETZ at the Duisburg meeting of the Deutsche Bunsen-Gesellschaft.* If the reaction



is carried out with a sphere of FeS in a stream of inert gas, containing SO_2 , the rate of reaction is determined by the diffusion through an outside porous layer of Fe_3O_4 . The diffusion proceeds in an outward gas flow because for every 4 SO_2 molecules which enter the reaction, 5 molecules of S_2 leave the interface $\text{FeS}/\text{Fe}_3\text{O}_4$, where the heterogeneous equilibrium according to (1) is assumed to be established. This diffusion problem can be treated without simplifications, as follows. Instead of (1) we use the general equation :



Where a solid S_1 reacts with a gas G_1 , and yields the solid S_2 and another gas G_2 , the number of moles μ of the newly formed gas may be greater or smaller than that of the consumed gas ν , corresponding to an outward or inward flow of gas.

In Fig. 1 ρ denotes the radius, r is the variable radius of the inner sphere of solid S_1 , and r_0 is the constant radius of the outer porous layer of solid S_2 . The speed of gas flow in the direction of $+\rho$ is v , depending on ρ , according to

$$v \rho^2 = v_0 r_0^2, v = v_0 \frac{r_0^2}{\rho^2} \quad (2)$$

if $v = v_0$ for $\rho = r_0$. The concentrations in the gas phase (within the porous material) are c_1 and c_2 for G_1 and G_2 , $c_1 + c_2 = c_0 = \text{const.}$ When

D is the effective diffusion coefficient for the porous material the diffusion flow is

$$J_D^1 = -D \frac{dc_1}{dp}; \quad J_D^2 = -D \frac{dc_2}{dp} = +D \frac{dc_1}{dp}. \quad (3)$$

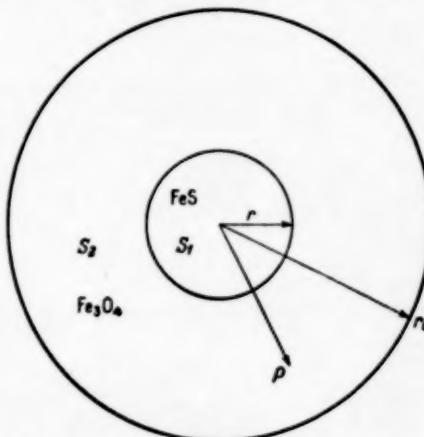


Fig. 1. Experimental set-up, used by MORAWIETZ, schematically, and notations.

The flow due to convection is

$$\begin{aligned} J_e^1 &= c_1 v = c_1 v_0 \frac{r_0^2}{\rho^2} \\ J_e^2 &= c_2 v = c_2 v_0 \frac{r_0^2}{\rho^2} \end{aligned} \quad (4)$$

and the total flow

$$J_1 = -D \frac{dc_1}{dp} + c_1 v_0 \frac{r_0^2}{\rho^2} \quad (5a)$$

$$J_2 = +D \frac{dc_1}{dp} + c_2 v_0 \frac{r_0^2}{\rho^2} \quad (5b)$$

$$J_1 + J_2 = (c_1 + c_2) v_0 \frac{r_0^2}{\rho^2}$$

* To appear in Z. Elektrochem.

The time-dependent diffusion equation for component 1 is

$$\frac{\partial c_1}{\partial t} = -\operatorname{div}(\mathbf{J}_1) = D \left[\frac{\partial^2 c_1}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial c_1}{\partial \rho} \right] - \frac{v_0 r_0^2}{\rho^2} \frac{\partial c_1}{\partial \rho} = 0 \quad (6)$$

which may be put equal to zero for a quasi-stationary state.

In this case c_1 depends on ρ only and we may write instead of (6)

$$\rho^2 \ddot{c}_1 + \dot{c}_1 (2\rho - \alpha) = 0 \quad (7)$$

where dashes denote differentiation with respect to ρ and we have introduced the length α

$$\alpha = v_0 r_0^2 / D \quad (8)$$

Equation (7) is to be solved for the following boundary conditions :

$$\text{for } \rho = r : \mu \mathbf{J}_1 = -v \mathbf{J}_2, c_1 c_2 \text{ according to equilibrium (1),} \quad (9a)$$

$$\text{for } \rho = r_0 : c_2 \approx 0 \text{ and} \quad (9b)$$

$$(\mathbf{J}_2)_{r_0} = (\mathbf{J}_2)_r \frac{r^2}{r_0^2} \quad (9c)$$

assuming that component 2 is carried away sufficiently quickly by the outside gas flow. From (9a) follows

$$\mu \left[-D \left(\frac{\partial c_1}{\partial \rho} \right)_r + c_1 v_0 \frac{r_0^2}{r^2} \right] = -v \left[D \left(\frac{\partial c_1}{\partial \rho} \right)_r + c_2 v_0 \frac{r_0^2}{r^2} \right]$$

and

$$D \left(\frac{\partial c_1}{\partial \rho} \right)_r = \left[\mu c_1 v_0 \frac{r_0^2}{r^2} + v c_2 v_0 \frac{r_0^2}{r^2} \right] / (\mu - v) \quad (10)$$

and from (9c), considering that $c_2 = 0$ for $\rho = r_0$:

$$D \left(\frac{\partial c_1}{\partial \rho} \right)_r \frac{r^2}{r_0^2} + c_2 v_0 = D \left(\frac{\partial c_1}{\partial \rho} \right)_{r_0}. \quad (11)$$

Putting c' in eq. (7) equal to ξ we have

$$\frac{d \log \xi}{d \rho} = \frac{\alpha - 2\rho}{\rho^2}, \quad (12)$$

and integrating between $\rho = r_0$ and ρ , we have

$$\log \frac{\xi}{\xi_0} = \frac{\alpha}{r_0} - \frac{\alpha}{\rho} - 2 \log \frac{\rho}{r_0}, \quad (13)$$

$$\xi / \xi_0 = (r_0 / \rho)^2 \exp(\alpha / r_0) \exp(-\alpha / \rho). \quad (13a)$$

By a further integration

$$c_1 - c_1^{r_0} = \int_{r_0}^{\rho} \xi d\rho = \frac{\xi_0 r_0^2}{\alpha} \times \exp(\alpha / r_0) \exp(-\alpha / \rho) - 1 \quad (14)$$

Eq. (13) gives $\left(\frac{\partial c_1}{\partial \rho} \right)_r$ ($= \xi$ for $\rho = r$) expressed by means of $\left(\frac{\partial c_1}{\partial \rho} \right)_{r_0}$. Substituting this in eqs. (10) and (11) we have two equations for v_0 and $\left(\frac{\partial c_1}{\partial \rho} \right)_{r_0}$, and with the values thus obtained we may calculate c_1 from (14). With $\rho = r$ and with α from eq. (8) eq. (13a) is written as follows

$$\left(\frac{\partial c_1}{\partial \rho} \right)_r = \left(\frac{\partial c_1}{\partial \rho} \right)_{r_0} \frac{r_0^2}{r^2} \exp \left(\frac{v_0 r_0}{D} \right) \exp \left(-\frac{v_0 r_0^2}{r D} \right) \quad (15)$$

and from eqs. (10) and (11)

$$D \left(\frac{\partial c_1}{\partial \rho} \right)_{r_0} = \mu v_0 (c_1' + c_2') / (\mu - v) \quad (16)$$

where c_1' and c_2' denote the concentrations for $\rho = r$. Further, from eqs. (11) and (15)

$$c_2' v_0 = D \left(\frac{\partial c_1}{\partial \rho} \right)_{r_0} \left[1 - \exp \left(\frac{v_0 r_0}{D} \right) \exp \left(-\frac{v_0 r_0^2}{r D} \right) \right], \quad (17)$$

and with (16)

$$c_2' v_0 = \frac{\mu v_0 (c_1' + c_2')}{\mu - v} \times \left[1 - \exp \left(\frac{v_0 r_0}{D} \right) \exp \left(-\frac{v_0 r_0^2}{r D} \right) \right]. \quad (18)$$

Solving (18) for the exponentials and taking logarithms we finally have

$$\frac{v_0 r_0}{D} - \frac{v_0 r_0^2}{r D} = \log \frac{\mu c_1' + v c_2'}{\mu (c_1' + c_2')} \quad (19)$$

and

$$v_0 = \frac{D}{r_0} \log \frac{\mu c_1' + v c_2'}{\mu (c_1' + c_2')} \cdot \frac{r}{r - r_0}. \quad (20)$$

Since $c_1^{r_0} = c_0$, the original concentration of 1 in the gas phase, and since c_1' is to be assumed as given by the concentration according to the heterogeneous equilibrium at $\rho = r$ for $S_1 + v G_1 = S_2 + \mu G_2$, $\zeta = c_1' - c_1^{r_0}$ is known, too. On the other hand, we have from (14)

$$\zeta = c_1' - c_1^{\infty} = \left(\frac{\partial c_1}{\partial \rho} \right)_{r_0} \frac{D}{v_0} \left[\exp \frac{v_0 r_0}{D} \exp \left(- \frac{v_0 r_0^2}{r D} \right) - 1 \right], \quad (21)$$

where v_0 is given by eq. (20). ζ and v_0 being known, (21) is an equation for $\left(\frac{\partial c_1}{\partial \rho} \right)_{r_0}$.

We now calculate the outward flow of component 2 through the outer surface at $\rho = r_0$. This is given, per unit area, by eq. (5b):

$$J_2 = D \left(\frac{\partial c_1}{\partial \rho} \right)_{r_0} (c_2 \text{ being zero at } \rho = r_0) \quad (22)$$

Substituting from eqs. (21) and (20) we find

$$J_2 = \frac{\zeta D r \log \frac{\mu c_1' + v c_2'}{\mu (c_1' + c_2')}}{r_0 (r - r_0) \left[\exp \left(\frac{v_0 r_0}{D} \right) \exp \left(- \frac{v_0 r_0^2}{r D} \right) - 1 \right]}. \quad (22)$$

From (23) with (19)

$$J_2 = \frac{\zeta D r}{r_0 (r - r_0)} \frac{\log \frac{\mu c_1' + v c_2'}{\mu (c_1' + c_2')}}{(v - \mu) c_2' / \mu (c_1' + c_2')}. \quad (24)$$

Eq. (24) assumes a particularly simple form for the special case $(v - \mu) c_2' \ll \mu (c_1' + c_2')$; in this case we write

$$\begin{aligned} & \log \frac{\mu c_1' + v c_2'}{\mu (c_1' + c_2')} \\ &= \log \frac{[\mu(c_1' + c_2') + \frac{1}{2}(v - \mu)c_2'] + \frac{1}{2}(v - \mu)c_2'}{[\mu(c_1' + c_2') + \frac{1}{2}(v - \mu)c_2'] - \frac{1}{2}(v - \mu)c_2'} \\ &= \log \frac{1 + (v - \mu)c_2' / [2\mu(c_1' + c_2') + (v - \mu)c_2']}{1 - (v - \mu)c_2' / [2\mu(c_1' + c_2') + (v - \mu)c_2']} \\ &\approx \frac{(v - \mu)c_2'}{2\mu(c_1' + c_2') + (v - \mu)c_2'} + \dots; \quad (25) \end{aligned}$$

using

$$\log \frac{1 + x}{1 - x} = 2 \left[x + \frac{x^3}{3} + \frac{x^5}{5} + \dots \right]. \quad (26)$$

Thus finally

$$J_2 \approx \frac{\zeta D r}{r_0 (r - r_0)} \frac{2\mu (c_1' + c_2')}{2\mu (c_1' + c_2') + (v - \mu) c_2'} \quad (27)$$

The total flux through the outside surface of area $4\pi r_0^2$ is

$$I = 4\pi r_0^2 J_2. \quad (28)$$

If d_1 is the density of phase 1, and d_2 density of phase 2, a change dr during time dt corresponds to a change dw in weight

$$dw = 4\pi r^2 dr (d_2 - d_1). \quad (29)$$

If in eq. (27) ζ , the concentration difference, is expressed in weight per cc., then (28) gives the total mass flow of component 2 out of the sphere. The rate of mass loss is obtained by multiplying this expression with $(\mu M_2 - v M_1) / \mu M_2$. Here M_1 and M_2 are the molecular weights of components 1 and 2, and use has been made of eq. (1). In the example quoted on the first page this expression is positive, but in other cases it might be negative as well. Thus we obtain from (28) and (29) :

$$\frac{dw}{dt} = \frac{\mu M_2 - v M_1}{\mu M_2} 4\pi r_0 J_2 \quad (30a)$$

$$= 4\pi r^2 (d_2 - d_1) \frac{dr}{dt}. \quad (30b)$$

There are several possibilities for a practical evaluation of experiments. One may integrate (30b) between the limits $t = 0$ ($r = r_0$, $w = w_0$) and $t = \tau$ ($w = w_\tau$, $r = r_\tau$), to give

$$w_0 - w_\tau = \frac{4\pi}{3} (r_0^3 - r_\tau^3) (d_2 - d_1). \quad (31)$$

When $w = w(t)$ has been measured as function of t , eq. (31) gives $r = r(t)$, as function of t . Inserting these values of r in eq. (30a), where J_2 depends on r according to (27), we obtain an expression for dw/dt , still depending on an arbitrary parameter D . If D can be adjusted in such a way as to fit the experimental values over a sufficient range of t , the problem has been solved, provided that the value of D is reasonable, i.e., corresponding to gaseous diffusion in a porous medium. Then the underlying assumption, that diffusion is the rate determining step, may be assumed as verified.

If, on the other hand, we want to calculate the time necessary for a certain amount of reaction, we write eqs. (30a) and (30b)

$$4\pi r^2 (d_2 - d_1) \frac{dr}{dt} = F(r) \quad (32)$$

$$F(r) = \frac{\mu M_2 - \nu M_1}{\mu M_2} 4\pi r_0^2 J_2$$

$$dt = \frac{4\pi r^2 (d_2 - d_1)}{F(r)} dr. \quad (32a)$$

Integrating (32a) between $t = 0$ ($r = r_0$) and $t = \tau$ ($r = r_\tau$) we finally obtain for the reaction time τ

$$\tau = \int_{r_0}^{r_\tau} \frac{4\pi r^2 (d_2 - d_1) dr}{F(r)}. \quad (33)$$

The integration is to be performed graphically. The value of the effective diffusion coefficient D must either be taken from former experiments or be estimated appropriately.

For a numerical evaluation of actual experiments we refer to MORAWIETZ' original paper. His method differs slightly from that presented here. The above calculations present a justification of his attempt to take into account the gas flow by introducing independent diffusion coefficients for both components.

NOTATION

| | |
|--|---------------------------------------|
| α = abbreviation for $v_0 r_0^2 / D$, of dimension of a length. | } |
| c_1, c_2 = concentrations of components 1 and 2 in the gas | |
| $c' = \partial c_1 / \partial \rho = \xi$. | [cm ² sec ⁻¹]. |
| D = diffusion coefficients | |
| G_1, G_2 = gaseous reactants, of concentrations c_1 and c_2 . | } |
| I = total flux of component 2 through outer sphere of area $4\pi r_0^2$. | |
| J = flow vector (mass passing in positive r -direction per unit time perpendicularly through unit area) indices 1 and 2 referring to components 1 and 2. | } |
| J_D = diffusion flow | |
| J_c = convection flow | |
| M_1, M_2 = molecular weights of components 1 and 2, respectively. | } |
| ν, μ = coefficients in reaction equation. | |
| ρ = radius, variable. | } |
| r = variable radius of inner sphere. | |
| r_0 = constant radius of outer sphere. | } |
| S_1, S_2 = solid reactants. | |
| v = flow velocity. | } |
| $\xi = c' = \partial c_1 / \partial \rho$. | |

The author would like to use this opportunity to correct a mistake overlooked in his book (*Diffusion in Solids Liquids and Gases*, Academic Press, New York, 1952) Eq. [1.237] on p. 54 should read

$$D [\frac{\partial^2 c}{\partial r^2} + (1/r) \frac{\partial c}{\partial r}] - \frac{v_0 r_0}{r} \frac{\partial c}{\partial r} = 0$$

one solution of which is $c = \beta r^{v_0 r_0 / D}$, with β arbitrary constant.

Hydroextraction VII : Residual moisture in whizzed cakes

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Summary—The consolidation of fine particulate beds due to compressive stresses makes it unlikely that a general relationship can be found for the de-watering of such hydroextractor cakes by whizzing, though empirical linear functions can be used for the effect of rotational speed on residual moisture content.

Résumé—Il ne paraît pas vraisemblable que l'on puisse établir une relation générale pour l'égouttage des gâteaux par le turbinage, à cause du tassement des lits de particules fines provoqué par les efforts de compression. Cependant des équations linéaires empiriques peuvent donner l'effet de la vitesse de rotations sur l'humidité résiduaire au cours de turbinage.

An important part of a hydroextraction cycle is the de-watering of the cake by "whizzing" without liquid being fed to the basket. The following studies were to assess the possibility of using simple correlation functions of appropriate variables such as surface tension and angular velocity to describe the variation of residual moisture content in cakes of fine particulate material. The initial compressibility of the cakes was also studied by observing the dependence of the moisture content of submerged cakes on hydroextractor speed on first running at successively higher speeds. The latter is of interest in assessing the packing rearrangements occurring in submerged cakes. The highest compression attained under these conditions is also of significance in the relationship between moisture content and whizzing speed in cakes running dry.

EXPERIMENTAL TECHNIQUE

In procedure A the granular material (chalk, maize starch or kieselguhr) was made to a thin slurry and fed to a 9 in. diameter hydroextractor basket with the precautions necessary to induce the formation of a smooth cake of vertical surface [1]. The centrifuge was spun at 900-1000 r.p.m., and thereafter for 15 minutes with the cake submerged under water. Without allowing the cake to run dry, the basket was stopped and samples of the cake taken out with an annular cutter of 1 in. diameter. Samples were cut from different circumferential positions and heights in the basket. Each sample was sliced into three

approximately equal parts to represent the inner, centre and outer radial positions of the cake. The weighed samples were dried at 105°C to constant weight.

Immediately after taking samples from the cake, it was run again submerged at a higher speed of rotation with the liquid inner surface being maintained at the same radius. After 5 minutes running at the new speed, samples were taken and treated in the same way as above. The procedure was repeated over the speed range of the hydroextractor.

In procedure B, after forming a cake in a hydroextractor basket, the speed was increased gradually up to the required value and maintained for 15 minutes with the cake still submerged. The liquid feeding was stopped and the cake was spun at a certain speed. Samples of complete cake thickness from mid-height were taken every minute, and their water content measured gravimetrically. It was found that 12 minutes was a reliable time of spinning for reaching a constant moisture content at different speeds and surface tensions.

In procedure C, after forming a cake and running it submerged at a certain speed, it was run dry (without liquid feed) for 12 minutes at the lowest speed, and samples were taken. The cake was then run at a higher speed, and sample taken, the procedure being repeated up to the highest speed (2800 r.p.m.).

In procedure D, a series of small cakes was formed by suction in a 1½ in. dia. cell [2] which was then mounted on the hydroextractor and

tested in the same way as mentioned in procedures B, C. Air was sucked through other samples in the small cell and the residual moisture contents obtained for comparison with the whizzing data from procedure B.

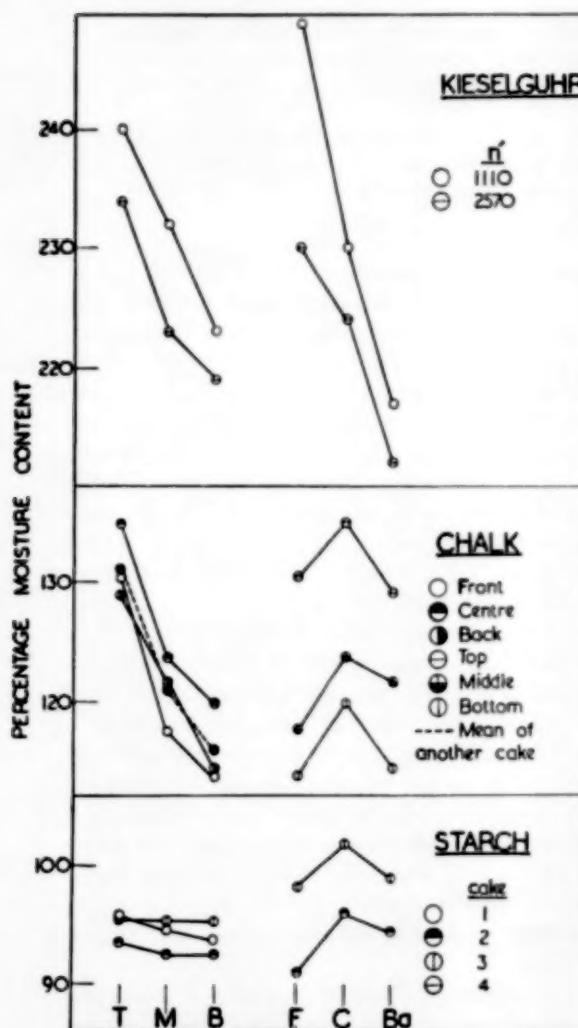


Fig. 1. Moisture content distribution in hydroextractor cakes ; (a) along the depth of the basket : T—top ; M—middle ; B—bottom ; (b) in a radial direction ; F—front, C—centre ; B—back.

Where possible the series were performed with maize starch, precipitated chalk and kieselguhr. To study the effect of surface tension Teepol was added to the formation and wash waters.

EXPERIMENTAL RESULTS : FOR WET CAKES

The "moisture content," R , of a sample is defined and used hereafter as the ratio of the liquid to dry solid in the sample, expressed as a percentage. This value is directly proportional to the void ratio in a sample which is completely submerged. The voids available to flow in a tightly packed fine solid may differ appreciably from the value appropriate to the above ratio.

Samples from either wet or spun-dry cakes gave reproducible moisture contents when taken at the same depth in the basket for any circumferential position.

The moisture content for samples from procedure A varied with the depth of basket, being always greater at the top. This variation was insignificant in case of starch cakes, whereas chalk and kieselguhr showed 10-15% higher moisture content at the top than at the bottom of the cake. The rate of change of moisture content with depth was higher in the top half of the basket, as shown in Fig. 1.

The radial distribution of moisture content passed through maxima in the cases of chalk and starch with the value at the inner radius slightly less than that at the outer radius (Fig. 1) and the maximum about 5% higher than the value at the inner radius. Kieselguhr showed a gradual decrease of water content from inner to outer radius (Fig. 1).

Chalk cakes formed under hydrostatic heads in the small cell did not show the type of variation noticed in cakes formed in the basket. The water content decreased 20% from front to back of the cake (Fig. 2, data : A). Samples formed by feeding to the spinning small cell and spun submerged gave similar moisture distributions such as the data B in Fig. 2. Agreement between the hydrostatic and spinning data was obtained from both chalk and starch cakes, showing that formation method has no influence on the packing. The maxima obtained in the distributions for hydroextractor cakes (Fig. 1) are thus indicative of packing characteristics peculiar to the hydroextractor cake.

The moisture content of samples from procedure A was independent of the speed at which a wet starch or kieselguhr cake was formed and washed.

The change was within 2% when the centrifugal stresses were increased six times (Fig. 17).

Chalk showed a gradual decrease of moisture content with spinning speed (Figs. 3 and 4). The water content after running at $n' = 2500$ r.p.m.

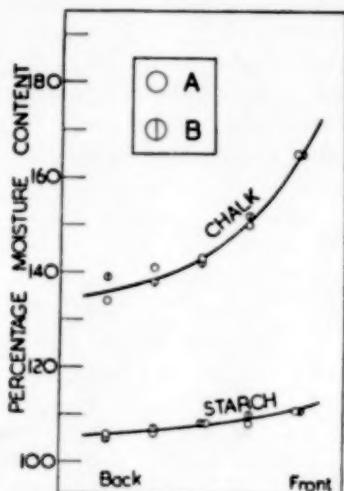


Fig. 2. Radial distribution of moisture content in cakes formed in the small cell; A : by feeding slurry to the spinning cell. B : by feeding slurry under hydrostatic suction head.

was 20% lower than after running at $n' = 1000$ r.p.m. The rate of change was of the same order at the inner, centre and outer radial positions of the cake, with the same distribution mentioned above (Fig 1) holding at most of the speeds. In some cases, however, the moisture content at the outer radius of the cake was higher than the middle, as at speeds the 800 and 1600 r.p.m. (Fig. 3). The test on the cake represented by the dotted curve B, Fig. 4 was repeated after attaining the highest speed. The difference b_1 represents the change due to altering the level of samplings, and the curve B_1 is the result of the repeated test. The condition attained after the original test was completed was hardly altered by repeating it, showing that the compression effect is not elastic. When Teepol was used to halve the surface tension of the formation liquid, the cake retained less water but the shape of curve remained the same (Fig. 4).

Although smooth curves may be drawn

through the experimental points on Fig. 3, 4, yet the abrupt changes cannot be ignored near the

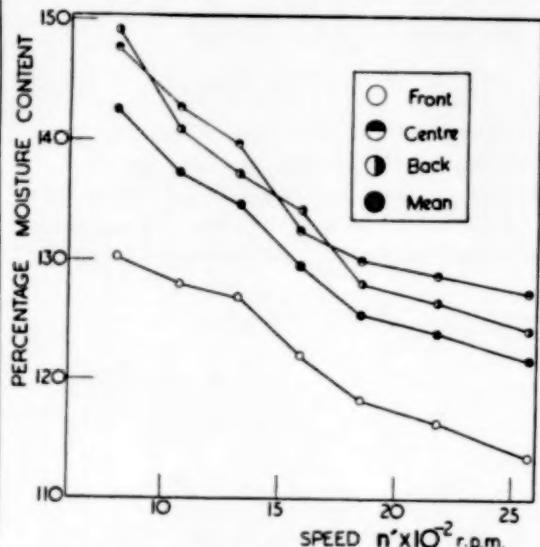


Fig. 3. Variation of moisture content with speed for a submerged chalk cake; samples from mid-height of the basket.

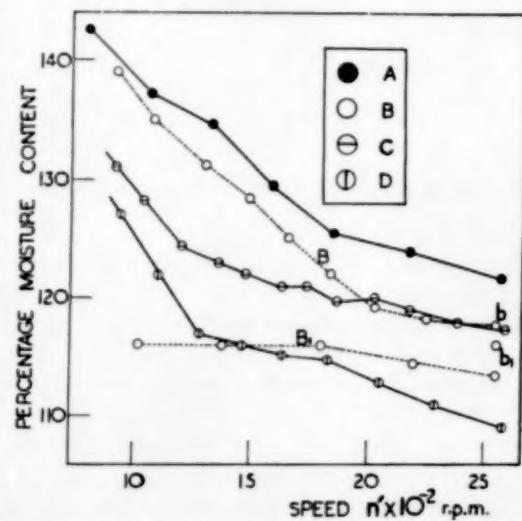


Fig. 4. Variation of moisture content with speed for submerged chalk cakes; "through" samples from mid-height of the basket; A, B, C : different cake thicknesses. B_1 : result of repeating test on cake B ; samples from top of the basket, b_1 represent the difference due to change of sampling height. D : cake containing the same weight of chalk as B and formed from water whose surface tension was lowered by an addition of Teepol.

speeds 1300 and 1800 r.p.m. On a semi-log plot (Fig. 5) these changes are clear.

The relation

$$R = R_0 - C \cdot \log_e n' \quad (1)$$

could represent the variation at different stages, with R_0 and C changing from stage to stage. It is most unlikely that equation (1) can be taken to represent a mean straight line through all the experimental points. The cake apparently suffers

assumption, the curves in Fig. 7 would not be changed whether drawn with R or the quantity representing (b) as ordinate.

The values (a), (c) are difficult to determine. If there is no evaporation during the process of spinning a cake dry, then the equilibrium value at the highest speed, R_m , will be mainly (a) and (c). Fig. 6 is a plot of $\log (R - R_m)$ against $\log n'$, and shows that the relation between void ratio and stress is not a simple power function. There is an apparent anomaly in that the

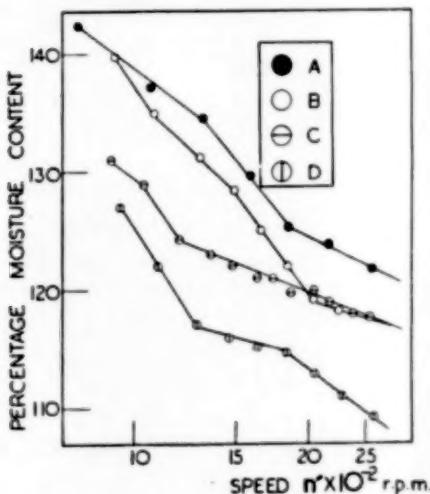


Fig. 5. Semi-logarithmic plot of the results in Fig. 4.

abrupt porosity changes caused by redistribution of the packed particles.

The water saturating a chalk bed will exist as :

- the equilibrium water content when submerged, i.e., water absorbed by the particles themselves,
- water filling the interstices between the particles and removable by flow,
- water held to the solid surface and not removable by flow.

The void ratio significant in flow phenomena is only dependent on (b) and a value representing the items (a) and (c) should be subtracted from the total water content in measuring the void ratio by moisture content. However, if (a) and (c) are considered constant, which is a reasonable

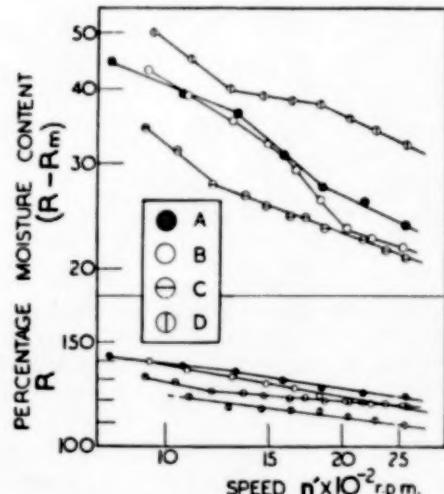


Fig. 6. Logarithmic plot of the results in Fig. 4.

curve for the cake formed from lower surface tension liquid is at higher ordinate than the others, leading to the conclusion that lowering the surface tension increases the porosity, which is contrary to the permeability result reported before. It is likely that during the dry running of the cake it is not only (b) that is affected, but (c), and perhaps (a) as well.

EXPERIMENTAL RESULTS FOR DRY CAKES

Whether cakes are dried by sucking air through them or by spinning, a certain time has to elapse before the moisture content reaches a constant value for a specific extractive force. Although the first few moments are the most effective in the process, yet the path of the curve cannot be

predicted due to apparent packing changes (Fig. 7). Twelve minutes is required for equilibrium to be reached in the cases represented in Fig. 7.

When the cakes were run dry, the distribution of water content from top to bottom of the cake remained similar to that when wet, but the radial distribution changes as shown in Fig. 8. The inner part was usually the driest in the cakes of kieselguhr and starch. Chalk reached constant dryness all through. With starch and kieselguhr a dry

the front layer forms a loose crust with starch and kieselguhr, which were materials unaffected by increased stresses when wet.

Figs. 9, 10, 11, 12 and 13 represent tests on one chalk cake formed from 1000 g dry chalk which was made to a thin slurry and fed to a hydroextractor rotating at 1000 r.p.m., then spun wet at 2000 r.p.m. Fig. 1 shows the wet condition of this cake. The data in Figs. 9-13 were obtained by procedure C. Increasing the speed of rotation when the cake is dry causes a movement of water

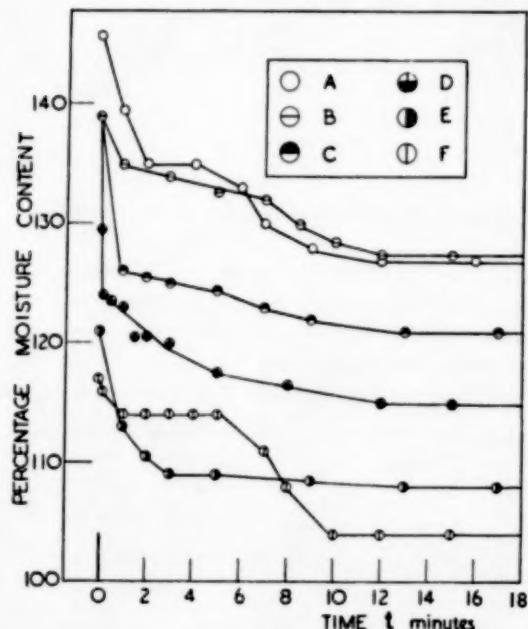


Fig. 7. Variation in residual moisture content with time : A : chalk cake formed in hydroextractor, washed with water and spun at 800 r.p.m. B : 5 g. chalk cakes formed by suction in small cell, washed with water and spun dry at 800 r.p.m. C : chalk cake formed from water-Teepol solution, in hydroextractor and spun at 1000 r.p.m. D : 5 g chalk cakes formed by suction in a small cell, washed with water and dried by sucking air through the cake. E : Starch cake formed in hydroextractor, washed with water and spun at 900 r.p.m. F : 5 g chalk cakes formed from water-Teepol solution, by suction in the small cell and dried by sucking air through the cake.

crust was observable at the inner radius of the cake. The material susceptible to increases in stress when running submerged, gave constant dryness across the cake, as with chalk, whereas

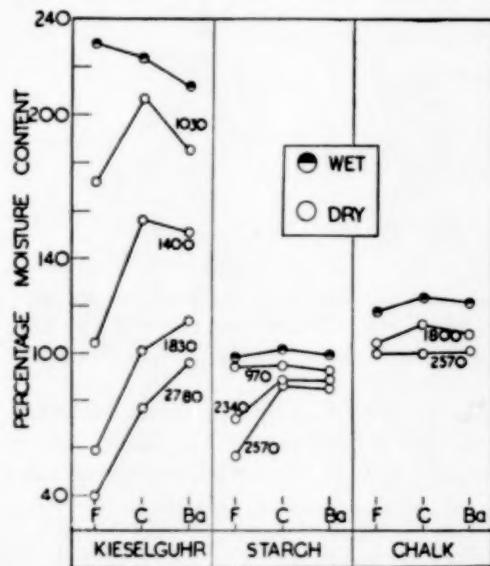
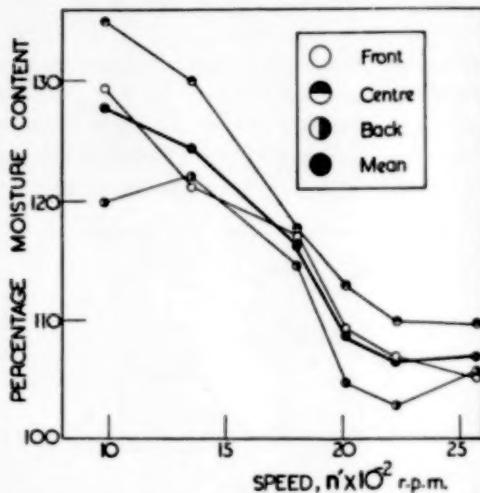


Fig. 8. Distribution of moisture content in wet chalk cakes, and in cakes dried at different speeds.

from the inner parts of the cake outwards, as well as a reduction of the mean water content. Thus, in Fig. 9, when the whizzing speed was increased from 980 to 1350 r.p.m., the mean water content of a "through" sample decreased, but water content at the inner part of the cake decreased more, while the outer part of the cake gained water. A similar effect is noticeable in other cases, such as at 2500 r.p.m. on Figs. 10 and 13.

The shape of drying curve is the same irrespective of the depth chosen for taking the samples (Fig. 12) or whether it is constructed from the mean moisture contents of the inner, centre or outer layers of the cake (Fig. 13).

Fig. 14 is the result of tests on a chalk cake which was run submerged at 2570 r.p.m. before the dry test. The highest speed running wet is referred to hereafter as the formation speed.



Figs. 9-13. Variation of residual moisture with speed of basket for a chalk cake formed at 2000 r.p.m. :

Fig. 9. Samples from the top of the basket.

The result of using Teepol to lower the surface tension of the formation and wash waters is shown in Fig. 15, the curve's shape remaining

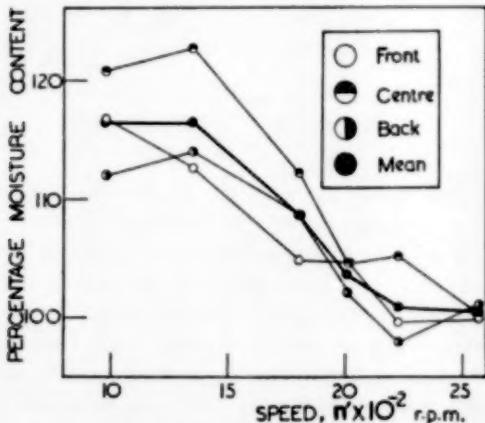


Fig. 10. Samples from the middle of the basket.

unchanged although the moisture contents are reduced. The effect of the formation speed on curve shape is illustrated in Fig. 16, which represents the mean of the water content of through

samples taken from the mid-height of cakes formed at different speeds. The formation speed abscissa coincides with a change in the effect of increasing the speed on the rate of cake drying

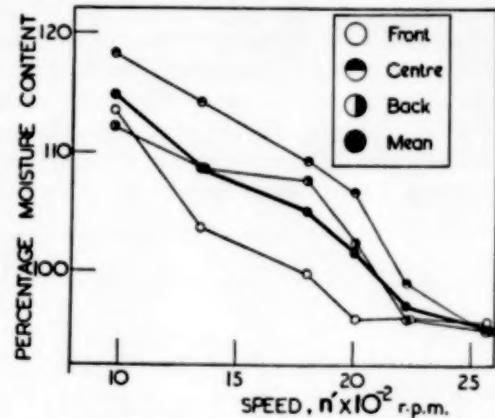


Fig. 11. Samples from the bottom of the basket.

and hence in the curve shape. The part before the formation speed is steeper and concave downwards, whereas thereafter the gradient decreases, the curve being convex to the abscissa axis. It seems that the cake starts a consolidation

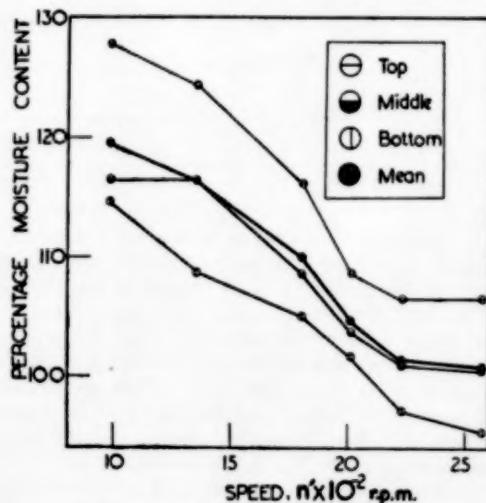


Fig. 12. Mean of "through" samples.

at this speed, which presumably results in lower porosity and greater ability for the cake to retain its water.

Curve B in Fig. 15 is from tests on cakes formed

in the small cell, spun wet at 2500 r.p.m., then spun dry at the prescribed speed for each sample. The form of curve is the same for the hydro-

gradual increasing moisture content distribution from inner to outer faces of the cake when run at higher speeds (Fig. 17). For comparison the broken curves are included, to indicate the slight changes with speed when running wet. Curve C in Fig. 17 is for a kieselguhr cake which was formed and washed at 1800 r.p.m., whereas the other curves are for a cake formed and washed at 2700 r.p.m. The formation speed had no

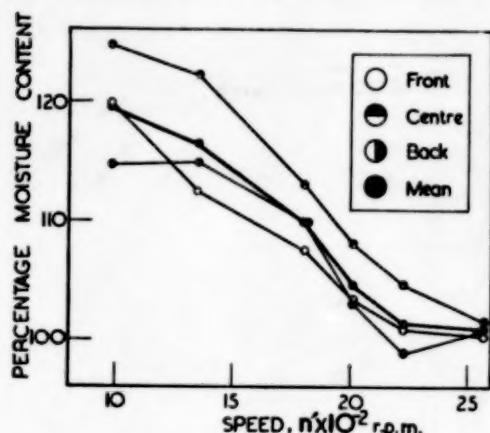


Fig. 13. Mean of different heights at same radial positions.

extractor cakes and small cell cakes, when spun dry at speeds below the formation speed.

The inner layer of the kieselguhr cakes always

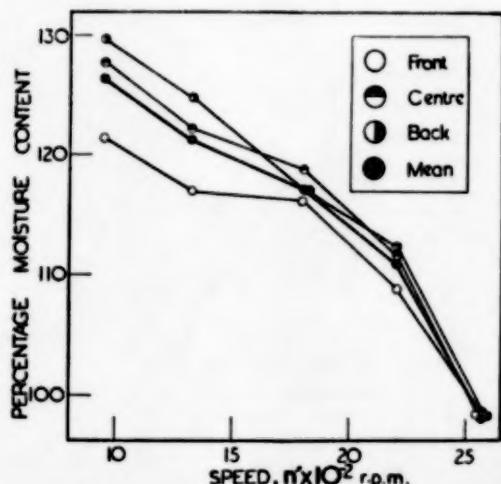


Fig. 14. Variation of residual moisture with speed on basket for a chalk cake formed at 2570 r.p.m.; sample from mid-height of basket.

contained less moisture than the rest of the cake. While the centre was of higher moisture content at the early stages of drying, it gave way to a

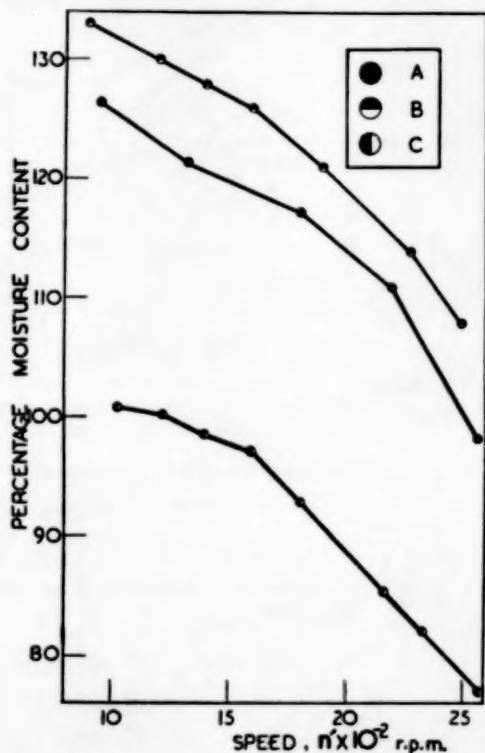


Fig. 15. Variation of residual moisture with speed for chalk cakes formed at 2570 r.p.m.; A : cake formed in hydroextractor from water. B : cakes formed in small cell from water. C : cake formed in hydroextractor from water-Teepol solution.

effect in this case, the invariable convexity to the abscissa axis suggesting that the kieselguhr always packs in the form similar to chalk above its formation speed.

When a starch cake was washed at 2500 r.p.m., then tested dry, the results in Fig. 18 were obtained. The change in the water content was insignificant up to a speed of about 2000 r.p.m.

where the cake began to dry rapidly, especially at the inner layer. When the surface tension of formation and wash water was halved by Teepol additions, the cake showed a similar drying behaviour (Fig. 19).

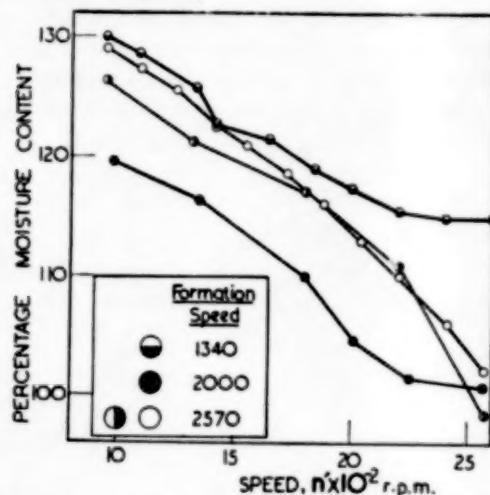


Fig. 16. Effect of formation speed on the variation of moisture content with speed of basket for cakes formed from different masses of chalk.

between centrifugal force and surface tension on the moisture retained on the surface of the packed material. Consider a mass $V(1 - \epsilon)\sigma$ of material of specific surface S and packed volume V spun

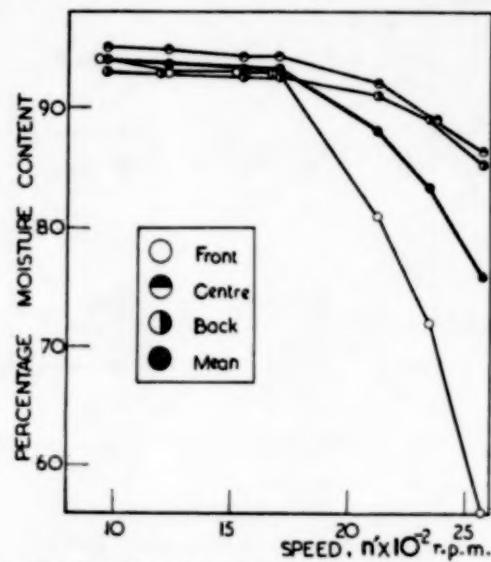


Fig. 18. Variation of moisture content with speed for a starch cake formed at 2500 r.p.m.

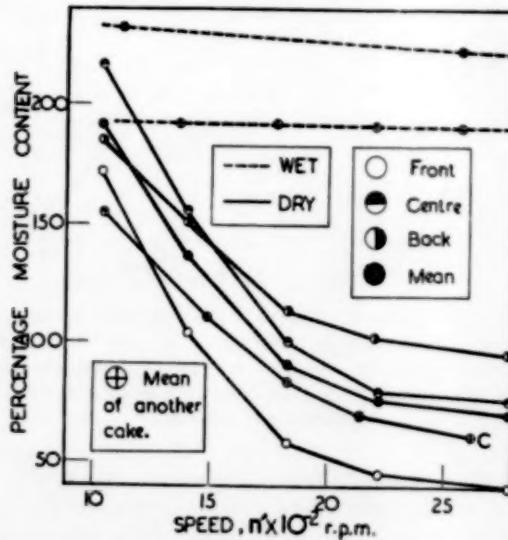


Fig. 17. Variation of moisture content with speed for kieselguhr cakes, submerged and dry.

The simplest consideration of the effect of rotational speed on residual moisture content in a whizzed cake may be based on the balance

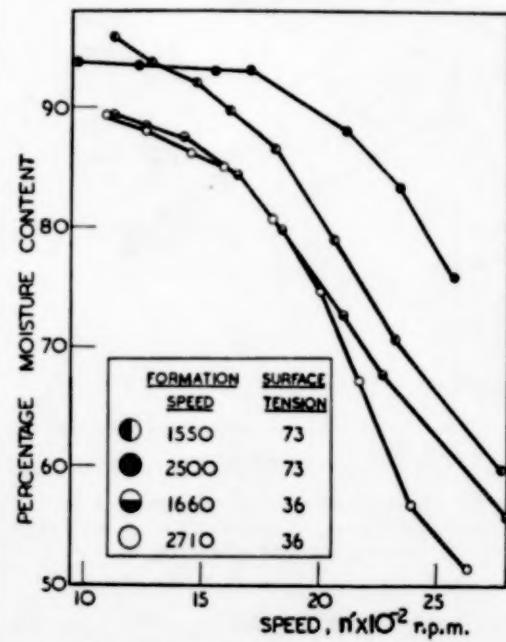


Fig. 19. Effect of formation speed and surface tension of formation solution on starch cakes.

at a mean effective radius r and angular velocity ω . The mean perimeter of the wetted surface in the bed is $[S V (1 - \epsilon) \sigma / L]$, if it is assumed that the surface can be characterised by a perimeter and effective length L . Then if the mass of liquid retained on the surface of the solid is m , the force balance gives

$$m = \frac{\gamma \cdot S V (1 - \epsilon) \sigma}{r \omega^2 L}$$

The liquid to solid ratio is given as

$$R = \frac{m}{V (1 - \epsilon) \sigma} = \frac{\gamma S}{r \omega^2 L}$$

or $R = \frac{\gamma S}{4 \pi^2 L n^2 r}$ (2)

If the solid absorbs water to give a residual content R_e , equivalent to the items (a) and (c) mentioned earlier, which cannot be extracted by centrifugal force; then the measured ratio R is given by

$$R = R_e + \frac{\gamma S}{4 \pi^2 r L n^2} \quad (2a)$$

This relation suggests that a plot of $(R - R_e)$ against $1/n^2$ should be a straight line passing through the origin of coordinates, if R_e is constant. This is not found to be so, the R data for chalk failing to conform to a simple power function of n , and the data for kieselguhr conforming to $R \propto (1/n)^y$, where $y = 1.0$ (Fig. 20).

In Fig. 20 data for chalk, kieselguhr and starch cakes formed at 2600 r.p.m. have been plotted as $\log (R - R_e)$ against $\log n'$, the value R_e being varied from zero to R_m , the residual moisture content for cakes spun dry at 2600 r.p.m. If $R_e = 0$, the plot should give a straight line from equation (2a) of gradient -2.0 . As R_e is increased, the gradient of the plot increases. A straight line of gradient -2.0 is not obtained within the range $0 < R_e < R_m$, probably due to the variation of L , R_e with n . Within the present experimental ranges of speed and cake geometry, it cannot be assumed that either R_m can be taken as R_e , or that any nominal value of R_e is likely to reduce the data to the desired straight line. The form of the curves in Fig. 20 suggest that

the variations of R_e and effective surface S vary sufficiently with compressive stress on the cake to render the equation (2a) valueless as a correlation function. The single effective length L is probably inadequate and should be replaced by a distribution function describing the effective mass and position of removable moisture.

It is possible to devise linear plots which may be of value in characterising a material. When the experimental results were plotted as $\log (R - R_e)$ against $\log (n_m' - n')$ for data at n' less than the formation speed, straight lines were obtained in the cases of chalk and kieselguhr

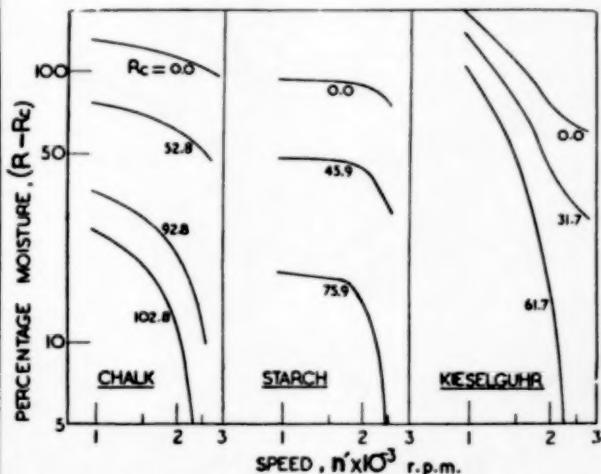


Fig. 20. Logarithmic plot of residual moisture content against speed for different R_e values varying from zero to R_m .

(Fig. 21). The equation representing these lines is

$$(R - R_m) = C \cdot (n_m - n)^x \quad (3)$$

whence

$$\frac{dR}{dn} = - C \cdot x (n_m - n)^{x-1} \quad (4)$$

when $x < 1$, the negative gradient dR/dn will increase with increasing n , as with chalk which has an R, n curve convex upwards (Figs. 14 and 15) for n below the formation speed. When $x < 1$; the negative gradient dR/dn decreases

with increasing n , which is the case with kieselguhr, the R, n curve being concave upwards with respect to the abscissa axis. Thus the same type of equation (3) can represent the cases of both chalk and kieselguhr cakes by straight lines in Fig. 21.

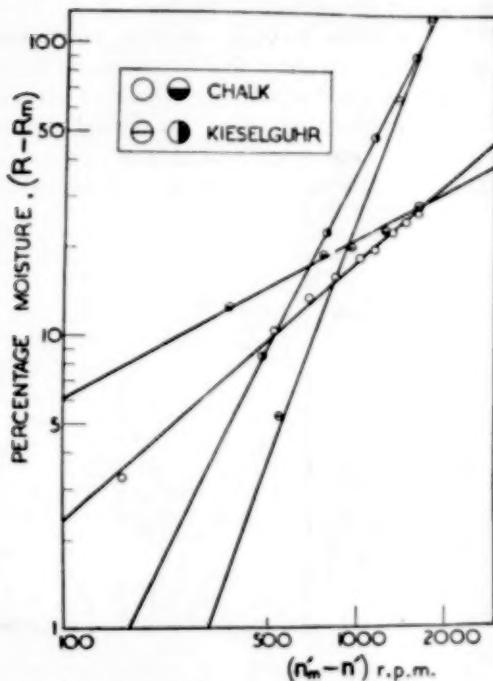


Fig. 21. Logarithmic representation of equation (3).

DISCUSSION OF RESULTS

The tests described above lead to the following conclusions :

It is unlikely that a general equation can be obtained to cover the changes in porosity occurring in a cake during its initial compression when submerged, as abrupt packing changes seem to occur.

It is unlikely that a general function can be derived for materials of the type studied to describe the de-watering of cakes by whizzing. When cakes are whizzed above their formation speed, defined as the highest speed attained when submerged, the drying curve differs from that for lower speeds, probably due to consolidation. The drying curves for specific materials running at

speeds below the formation speed may be represented by empirical equations such as equation (3) which lead to linear plots of possible value. The speed range below the formation speed is the probable range of interest.

The apparent compressive effects and packing distributions make it impossible to use a simple surface tension function for correlating de-watering data, even when using data from mean positions in hydroextractor cakes.

The porosity distributions considered proportional to the moisture distribution in submerged cakes pass through maxima in a radial direction, suggesting that the permeability thus does not follow a smoothly decreasing porosity with increasing radius. Though the methods of cake formation in small cells and hydroextractor baskets show little influence on the mean permeabilities [2], the porosity distributions may differ. The data in Fig. 2 show that formation mechanism has no effect in the small cell, differing from the results in the hydroextractor. The latter are probably dependent on whether the cake is formed by a multi-layer technique. Though the permeability differs in vertical and horizontal position even in cakes of fine particulate material, it seems adequate to assess cakes in terms of the mean values in practice.

NOMENCLATURE

| | |
|--|--------------|
| L = effective length of packed sample | cm |
| m = mass of water in sample | g |
| n = speed of revolution : n_m maximum test speed ; (rev. per sec.) ; n' rev. per min. | |
| R = moisture content taken as ratio of water to solid in cake ; R_m minimum content attained at highest test speed ; R_e residual content. | |
| r = radius from axis of rotation | cm |
| S = effective specific surface of packed material | sq. cm/g |
| V = volume of packed sample | cc |
| γ = surface tension | dyne/cm |
| ϵ = porosity of packed bed | |
| σ = density of solid | g/cc |
| ω = rotational speed | radians/sec. |

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Le réacteur étagé—outil fondamental de Génie Chimique

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Summary—The continuous flow stirred tank reactor (C.F.S.T.R.) is especially suited for the experimental study of reaction kinetics in homogeneous systems; the steady conditions achieved in the reactor are connected directly to the laws of chemical change and not through a differential equation. Experimental determination of the steady state can be performed with increased accuracy.

In many cases, kinetics in a C.F.S.T.R. remain independent of the geometrical shape; the results can be readily extrapolated for industrial design. A convenient graphical method is proposed for the accurate determination of the optimum volume ratio between the various compartments. While the conditions at the start or the stop of the reactor remain very difficult to establish by theory, with a laboratory model their determination by direct experimentation is very easy.

A convenient design of laboratory set-up is proposed. Preliminary results confirm that such a type of equipment will be very useful for the development of chemical engineering kinetics.

Résumé—Développant la théorie du réacteur étagé continu de DENBIGH, l'auteur insiste sur les avantages de cet appareil pour l'étude expérimentale de la cinétique d'une réaction homogène: l'état stationnaire réalisé dans chaque étage reste une fonction directe au lieu d'une fonction différentielle de la loi cinétique. La détermination expérimentale de cet état stationnaire peut être rendue très précise.

Dans bien des cas, les résultats du réacteur étagé sont indépendants de la forme géométrique: ils sont alors directement extrapolables à l'application industrielle. L'auteur présente une méthode graphique commode et précise pour le calcul du volume optimum des divers étages. Tandis que l'établissement théorique de la mise en régime ou de l'arrêt reste toujours très pénible, l'essai au Laboratoire permet de préciser aisément toutes les circonstances accompagnant les états transitoires.

L'auteur propose finalement un type simplifié de réacteur de laboratoire dont les résultats justifient l'intérêt de ce type d'appareil pour les études de Génie Chimique.

Le calcul des appareils industriels peut être considérablement simplifié si on étend la notion d'opération fondamentale aux appareils eux-mêmes, plutôt qu'à la nature chimique de la réaction qui s'y produit. Mais ce calcul exige toujours un assez grand nombre de données thermodynamiques et cinétiques; la découverte et l'utilisation industrielle constante de nouveaux produits font que ces données sont très fréquemment manquantes. Les méthodes d'approximation sont d'un certain secours, mais ne sont jamais qu'un pis aller, et sont inapplicables ou inexistantes dans bien des cas (surtout en cinétique chimique).

Le problème se pose donc, et de façon sérieuse, de savoir comment l'Ingénieur va se procurer les données indispensables au *calcul des processus d'échanges intra-moléculaires*.

Nous nous proposons ici d'examiner un type d'outil qui nous a paru spécialement propre à certaines études de Génie Chimique, de montrer en quoi il est spécialement apte à fournir des données nécessaires à toute une série de calculs industriels, et nous proposerons un modèle type d'appareil peu coûteux et d'une précision suffisante.

La théorie du réacteur étagé (en anglais: Continuous flow stirred tank reactor) a été établie par DENBIGH [1].

* Tué accidentellement le 23 Septembre, le Professeur V. R. LECLERC n'a pu revoir lui-même les épreuves de l'article que nous publions. Les éditeurs déplorent cet accident qui prive l'Université Française d'un chercheur passionné des problèmes du GENIE CHIMIQUE; ils s'excusent des erreurs que la mort de l'auteur n'a pas permis de corriger dans le texte ci-dessous.

Rappelons le principe de l'appareil. Le réacteur étagé est constitué par un certain nombre d'étages (Fig. 1) alimentés en continu, et débitant en con-

le passage direct de l'étude de laboratoire à la réalisation industrielle. Nous allons examiner ces deux aspects.

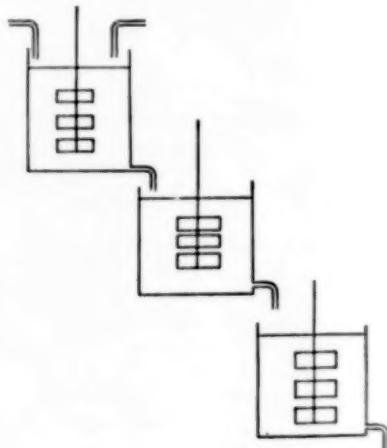


Fig. 1.

tinu, à débit constant et égal pour chaque étage. Chaque étage est isotherme et muni d'un puissant agitateur. Si nous laissons de côté le cas des réactions à pression constante et volume variable, les conditions qui suivent sont nécessaires et suffisantes pour que chaque étage puisse être caractérisé chimiquement par un régime permanent et une composition homogène (qui est la composition à la sortie) :

- Constance des débits d'entrée et de sortie,
- Constance du volume occupé par le fluide dans l'étage (égalité des entrées et des sorties),
- Agitation suffisante pour que le temps de mélange soit petit devant le temps de passage,
- Constance et uniformité de la température.

Si, par ailleurs, la réaction n'est pas influencée par les parois, il est évident que toutes les conditions ci-dessus peuvent être réalisées indépendamment de la forme ou des dimensions de l'étage.

Cette caractéristique du réacteur étagé fait qu'il constitue un appareil de choix pour la détermination des constantes cinétiques et, en même temps, un outil fondamental d'études de Génie Chimique, particulièrement apte à faciliter

DETERMINATION DES CONSTANTES CINETIQUES

L'étude d'une réaction en solution exige des déterminations :

- De l'ordre de réaction (à l'origine et en fonction de l'état d'avancement),
- De la constante de vitesse,
- De l'influence de la constante diélectrique du solvant et de la force ionique.

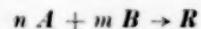
Ces déterminations se ramènent finalement à des mesures de composition chimique et de temps.

La plupart des données de la littérature proviennent de déterminations faites avec un réacteur simple (batch process). Lorsqu'il s'agit d'une réaction en solution, on opère généralement sur un volume de liquide assez grand, obtenu par mélange rapide de deux réactifs.

Pour suivre la composition en fonction du temps, on effectue, à des intervalles de temps choisis, des prélèvements qu'on analyse (sauf le cas relativement rare où on peut suivre en continu la composition par une méthode physique). Ces prélèvements sont fréquemment effectués à l'aide d'une pipette. Il résulte de ce mode opératoire une incertitude assez grande tant sur l'origine des temps que sur la "date" des prélèvements. De plus, l'interprétation des résultats sera assez difficile si la réaction est d'ordre fractionnaire et si la force ionique varie au cours de la réaction (5-16).

Nous voulons montrer que le réacteur étagé offre sur le réacteur simple des avantages notables quant à la précision et à la simplicité des déterminations.

Considérons une réaction (irréversible pour simplifier)



d'ordre α par rapport à A et d'ordre β par rapport à B c'est-à-dire dont la vitesse obéit à la loi :

$$-\frac{da}{d\theta} = k a^\alpha b^\beta$$

où a et b représentent les concentrations instantanées en A et B .

Il s'établira dans chaque étage un état stationnaire correspondant à des concentrations $a_1, a_2 \dots a_n$ et $b_1, b_2 \dots b_n$. L'alimentation du réacteur est caractérisée par des concentrations a_0 et b_0 . Soit F le débit de cette alimentation, $V_1, V_2 \dots V_n$ les volumes des étages.

Il entre dans le 1er étage, par unité de temps, $a_0 F$ moles de A et il en sort, dans le même temps, $a_1 F$. La différence est $F(a_0 - a_1)$ pour le volume V_1 , et par unité de volume $F/V_1(a_0 - a_1)$ pour le 1er étage. Pour le n ème étage, cette différence devient $F/V_n(a_{n-1} - a_n)$.

La différence entrée - sortie est égale au nombre de moles de A disparues par unité de temps et unité de volume, du fait de la réaction. Pour l'étage 1 de concentrations stationnaires a_1 et b_1 , elle est par définition :

$$-\frac{da}{d\theta} = k a_1^\alpha b_1^\beta$$

D'où les relations, pour l'étage 1 :

$$\frac{F}{V_1} (a_0 - a_1) = k a_1^\alpha b_1^\beta$$

pour l'étage n (si l'ordre ne varie pas) :

$$\frac{F}{V_n} (a_{n-1} - a_n) = k a_n^\alpha b_n^\beta$$

Ce type d'équations contient des grandeurs à déterminer expérimentalement et les inconnues k, α, β . Ceci permet, au prix d'un nombre convenable d'expériences de déterminer l'ordre (même fractionnaire), et la constante de vitesse. DENBIGH [1] a fait remarquer l'intérêt de ce type d'équation : il n'y a pas à effectuer d'intégration, avantage considérable pour les réactions complexes.

Par ailleurs, la précision du maintien de l'état stationnaire peut être très élevée (meilleure que 0.1%) car elle ne dépend que du réglage des débits et d'une agitation suffisante ; tout se passe comme si la réaction était "gelée" à un état donné. La précision des mesures de concentration peut également être très élevée puisqu'il est possible d'effectuer autant de prélèvements que l'on veut pour définir l'état permanent - on peut donc faire la moyenne de nombreuses analyses chimiques. D'autre part, le temps correspondant au prélèvement est ici le

rapport V/F du volume occupé au débit de l'alimentation. Ce temps peut être déterminé statistiquement et non par une seule mesure comme dans un réacteur simple.

Enfin, en recevant le liquide sortant de l'appareil dans un récipient contenant un réactif convenable, il devient possible d'arrêter instantanément la réaction. D'autre part, le réacteur étagé permet de choisir, et de maintenir constantes, diverses conditions opératoires qui influent sur la vitesse de réaction. DENBIGH [1] écrit à ce sujet :

"La réaction peut être étudiée dans des conditions rigoureusement constantes de concentration en catalyseur (ou en radicaux libres) ou de force ionique, et ceci à n'importe quel stade de la réaction."

Precisons que la force ionique peut être maintenue constante non seulement dans chaque étage considéré individuellement, mais dans l'ensemble des étages. Il suffit pour cela d'effectuer des additions convenables d'ions à chaque étage. On peut ainsi, du début à la fin, étudier une réaction à force ionique constante, et choisie, ce qui est pratiquement impossible avec un réacteur simple.

Il semble, à première vue, que nous venons d'énumérer des avantages qui appartiennent non au réacteur étagé mais aux réacteurs continus en général ; c'est-à-dire qu'on pourrait aussi bien utiliser un réacteur tubulaire pour cette étude cinétique. Mais le réacteur tubulaire présente des inconvénients très graves. En effet, il est facile de montrer que pour un tel type de réacteur, fonctionnant en régime laminaire, chaque tranche mince est caractérisée par un état stationnaire mais cet état stationnaire n'est pas homogène. (Le réacteur tubulaire est par contre un instrument intéressant pour déterminer commodément le degré d'influence des parois.)

PROJET D'APPARILLAGE INDUSTRIEL

Dans ce qui précède, nous avons montré que le réacteur étagé, à un ou plusieurs étages, est un outil de choix pour la détermination des constantes cinétiques. Il reste encore l'outil de choix pour les études de Génie Chimique destinées à permettre par extrapolation la réalisation industrielle d'une réaction étudiée au laboratoire.

Dans le cas d'une réaction effectuée dans un réacteur étagé, le problème immédiat est la détermination du volume des étages et de leur nombre. De plus, il faut prévoir les conditions de mise en régime et d'arrêt de l'appareillage. Nous avons déjà insisté sur le fait que *toutes les conditions caractérisant le fonctionnement du réacteur à étages sont indépendantes de la forme ou des dimensions des étages*. L'appareil de laboratoire est directement transposable aux dimensions exigées par le tonnage de fabrication envisagé.

Calcul des dimensions du réacteur

ELDRIDGE et PIRET [4] ont donné une méthode graphique qui permet de calculer le nombre des étages nécessaires à réaliser une réaction donnée (V/F étant fixé) ou de calculer le rapport V/F si on se fixe le nombre des étages. Mais pour des raisons de commodité, il se sont limités au cas du réacteur à n étages identiques.

L'intérêt qu'il y a à faire varier le volume relatif des étages d'un réacteur industriel n'ayant pas, à notre avis, été suffisamment mis en lumière, nous commencerons par montrer cet intérêt, avant d'indiquer les ressources du réacteur étagé de laboratoire pour le calcul de l'appareil industriel.

Il est possible d'obtenir un gain de rendement si on accroît le volume des étages à mesure que la réaction progresse (ce qui revient à accorder davantage de temps à une réaction qui se ralentit).

Soit une réaction irréversible $A + B \rightarrow R$ d'ordre 2 avec concentrations initiales égales $a_0 = b_0$. La méthode du bilan matériel indiquée précédemment permet d'établir les équations des deux premiers étages :

$$k \frac{V_1}{F} a_1^2 + a_1 - a_0 = 0 \quad (1)$$

$$k \frac{V_2}{F} a_2^2 + a_2 - a_1 = 0 \quad (2)$$

les étages suivants étant également caractérisés par d'autres équations du 2ème degré, la constante de chacune d'elles étant la racine de la précédente.

DENBIGH [1a] a fait remarquer que si on néglige le terme a_1 de l'équation (1) et le terme

a_2 de l'équation (2) il est facile de tirer une valeur de a_2 qui est :

$$a_2 = \left(\frac{F_2 a_0}{k^3 V_1 V_2^2} \right)^{0.25}$$

expression qui passe par un minimum (correspondant à un maximum de rendement) si $V_2 = 2V_1$

- Pour une réaction d'ordre 3, on aurait $V_2 = 3V_1$
- En première approximation le rapport optimum des volumes serait celui de l'ordre de la réaction.

Nous avons cherché à établir une méthode commode et précise de détermination de cet optimum et nous nous sommes arrêtés à une solution graphique. L'équation 2 peut s'écrire :

$$a_1 = k \frac{V_2}{F} a_2^2 + a_2 \quad (3)$$

et l'équation (n) serait :

$$a_{n-1} = k \frac{V_n}{F} a_n^2 + a_n \quad (4)$$

Ces équations font apparaître une relation linéaire entre le volume V d'un étage considéré et la concentration à laquelle on l'alimente (F étant fixe) si nous nous imposons la concentration de sortie.

Il est alors possible de tracer une famille de droites divergentes qui exprimeront des relations linéaires entre V/F et la concentration d'alimentation ceci pour diverses concentrations fixes de sortie.

Supposons que nous voulions pour la réaction précédente réaliser la transformation de A de la concentration 0.7 à la concentration 0.5 en 2 étages. Considérons la Fig. 2. La droite D_1 représente l'équation :

$$a_1 = k \frac{V_2}{F} 0.5^2 + 0.5$$

et le point I correspond à une valeur de V/F qui impose une concentration d'alimentation 0.52.

Si nous menons par ce point une parallèle à la droite D_2 ($a_0 = k V_1/F \cdot 0.52^2 + 0.52$) nous atteignons l'ordonnée 0.7 au point I' dont l'abscisse donne pour V/F la valeur correspondant au temps total de séjour pour réaliser la conversion de 0.7 à 0.5. Si nous recommençons l'opération en nous arrêtant au point II d'abscisse 0.54 nous

tracerons une parallèle à la droite D_3 ($a_0 = K \frac{V}{F} 0.54^2 + 0.54$) et nous atteindrons l'ordonnée 0.7 en un point II' dont l'abscisse est plus faible que celle du point I'. Si nous continuons à faire croître les temps de passage alloués au dernier étage, nous verrons que le point final passe par une abscisse minimum, ce qui fixe le rapport optimum des 2 étages.

Si, par convention, nous prenons pour unité les concentrations initiales a_0 et b_0 , nous obtiendrons, en cinq essais, les valeurs suivantes pour les temps de passage *relatifs* à travers deux étages successifs :

| Temps de passage | | |
|--|--|---------------------------------|
| 2 ^e étage (V/F) ₂ | 1 ^e étage (V/F) ₁ | total (V/F) _t |
| 240 | 447 | 687 |
| 320 | 358 | 678 |
| 360 | 315 | 675 |
| 400 | 245 | 675 |
| 440 | 243 | 683 |

Le tracé de la courbe $(V/F)_t$ en fonction de $(V/F)_2$ donne pour valeur minimum $(V/F)_t = 674$ avec $(V/F)_2 = 380$ et $(V/F)_1 = 294$ ce qui correspond à un rapport optimum d'environ 1.3.

La même opération effectuée avec une réaction d'ordre 3 donne 1.7 environ pour le rapport optimum des valeurs de sorte que le rapport optimum du volume des étages varie à peu près comme la racine carrée de l'ordre de la réaction.

Il est facile de vérifier la position du minimum en comparant un réacteur à étages égaux, un réacteur à étages inégaux et un réacteur tubulaire. Il n'y a qu'à appliquer les formules classiques pour le réacteur tubulaire, et la série d'équations du 2^{ème} degré pour n étages égaux ou inégaux.

La Figure 3 donne un exemple de cette comparaison.

Cette méthode est évidemment générale, pourvu que l'on connaisse l'ordre et la constante de vitesse de la réaction ; il reste encore possible de l'appliquer si l'ordre et la constante de vitesse varient au cours de la réaction, soit de par la nature de la réaction, soit à cause d'additions variées.

On peut choisir des conditions opératoires aussi complexes que l'on veut (choix dicté par des études cinétiques préalables). L'usage d'un réacteur étage de laboratoire permettra toujours de déterminer, pour une zone peu étendue de

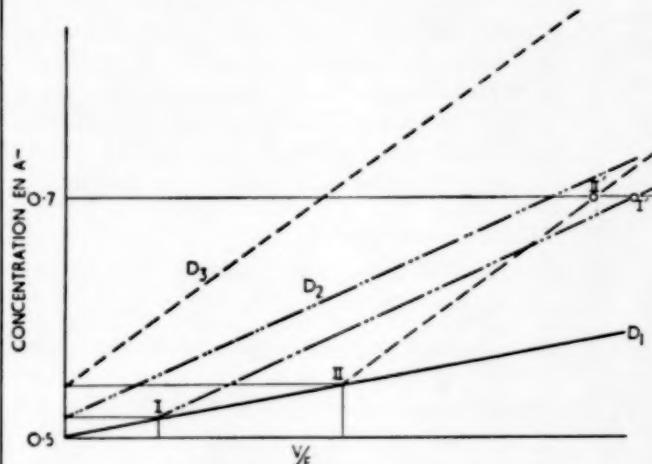


Fig. 2. Schéma de la méthode graphique pour calculer le rapport optimum des volumes des étages.

conditions opératoires, la loi de variation des coefficients cinétiques ; il permet évidemment de déterminer graphiquement le rapport de

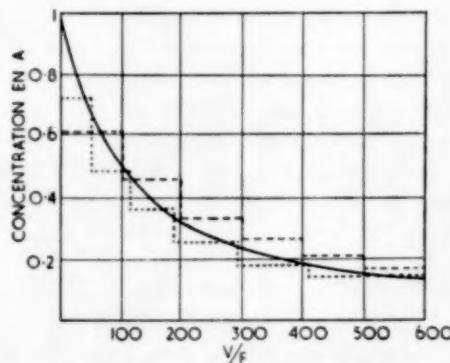


Fig. 3. Comparison du réacteur tubulaire — .
Comparaison du réacteur étage (étages égaux) — — .
Comparaison du réacteur étage (étages inégaux)
Réaction $A + B \rightarrow R$. $a_0 = b_0$. $k = 10^{-2}$.

volumes convenant à ces conditions complexes et de vérifier, au laboratoire, ce que donneront les appareils industriels.

Une fois établi à l'aide des données de laboratoire, le graphique permet de choisir le nombre d'étages nécessaires ; ce choix dépendra des contraintes que l'on s'imposera par des considérations d'ordre économique. Dans beaucoup de cas, partant d'une concentration initiale donnée, il suffit d'aboutir à une concentration finale, plus ou moins rigoureusement imposée : le graphique permet la détermination du nombre d'étages à choisir ; il montre immédiatement les avantages que présentent des étages inégaux pour contrebalancer les complications dans la construction.

Mise en marche et arrêt

Pour mettre un réacteur étagé en marche, on peut utiliser procédés divers :

- Tous les étages sont remplis par un fluide inert ou par le solvant pur,
- On remplit chaque étage avec l'alimentation initiale,
- On remplit chaque étage en y mélangeant des solutions titrées de façon à produire la composition prévue pour l'état stationnaire.

De toutes façons, la prévision de l'atteinte de l'état stationnaire (nécessaire pour savoir ce qui sortira de l'appareil pendant ce temps) présente très vite de grosses difficultés mathématiques (voir à ce sujet PIRET et MASON [2]).

Les qualités d'extrapolation du réacteur de laboratoire permettent une prévision complète des compositions chimiques pendant la mise en marche et l'arrêt, dans des conditions en principe aussi compliquées que l'on veut (toujours bien entendu si la paroi de l'appareil est inactive chimiquement).

REACTEUR ETAGE DE LABORATOIRE

Les considérations précédentes nous ont amené à considérer comme un problème très intéressant celui de la réalisation d'un bon réacteur de laboratoire. Divers modèles ont déjà été proposés en particulier celui de DENBIGH [3] et celui de PIRET et ELDRIDGE [4]. Ces modèles ont pour caractéristique d'être entièrement clos pour permettre une connaissance exacte du volume de l'étage.

Nous avons cherché à établir un modèle ouvert,

peu coûteux à réaliser, facile à manipuler et de précision suffisante. Mais pour justifier les considérations énoncées plus haut nous avons choisi parmi plusieurs modèles possibles celui qui avait la forme la plus différente des modèles déjà décrits : le modèle retenu est en fait un tube de Thiele agrandi.

La Figure 4 donne les caractéristiques essentielles de sa construction. Si la tige de l'agitateur

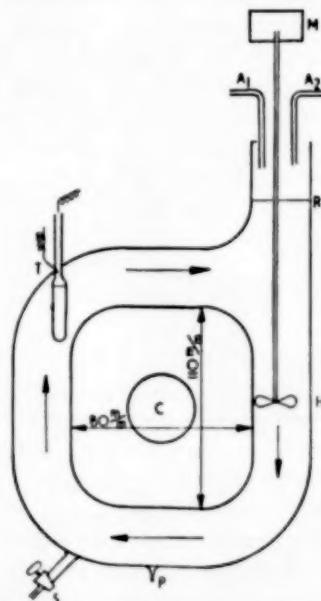


Fig. 4. Corps en pyrex 30/34 mm.
 A_1, A_2 Alimentation par vases de Mariotte.
 C Chauffage par rayonnement.
 T Thermo régulateur à mercure-Soudé.
 H Hélice 4 pales, arbre $\phi = 4$ mm.
 R Repère gradué ($V = 340$ cc).
 S Robinet de déversement dans le 2ème étage.
 P Poupe capillaire pour prélevements en cas de fonctionnement à plusieurs étages.

est assez fine, il n'y a pas formation de vortex appréciable et on peut s'assurer de la constance du volume comme pour une fiole jaugée. Le fonctionnement de l'appareil a été soumis aux vérifications expérimentales suivantes :

(a) *Agitation*—La rapidité d'homogénéisation a été vérifiée par remplissage de l'étage avec une solution de soude caustique $N/5$ et addition d'une

goutte de phénol phtaléine, (on peut utiliser toute réaction colorée instantanée) et par addition à de l'eau distillée de bleu de méthylène concentré.

Le temps de mélange est de 8 secondes $\pm \frac{1}{2}$ seconde, ce qui est suffisamment petit pour utiliser des temps de passage de l'ordre de 300 secondes et plus.

(b) *Débits*—La constance des débits des vases de Mariotte et du réacteur a été vérifiée par remplissage chronométré de fioles jaugées.

Le débit en cc./minute est d'une bonne reproducibilité (écart type de 0.2%).

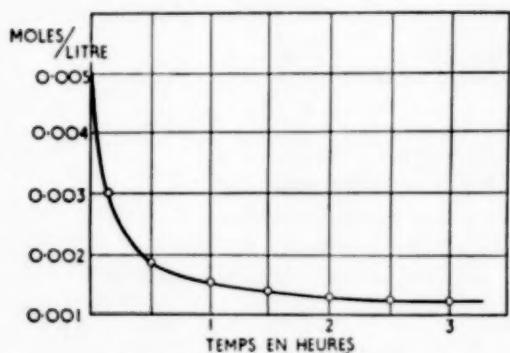


Fig. 5. Atteinte de l'état stationnaire.
 $[\text{NaOH}]_0 = 0.00498$ moles/litre. $(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5) = 0.225$
 Temps de passage = 22 min.

Pour les premiers essais effectués à 25°C des moyens très simples suffisant à régler la température à $\pm 0.1^\circ\text{C}$. Ces premiers essais regardés comme satisfaisants, nous avons essayé l'appareil en y réalisant une réaction connue.

Nous avons choisi la saponification de l'acétate d'éthyle en solution diluée, réaction dont la constante de vitesse a été établie par des travaux classiques, et chose intéressante, vérifiée par DENBIGH [3] avec un modèle fermé de réacteur étagé.

Les analyses ont été faites en pesant des quantités données du produit sortant, reçu dans de l'acide chlorhydrique titré $N/100$ et titrant l'excès d'acide en présence d'indicateur de neutralité.

La Figure 5 donne la courbe d'atteinte de l'état stationnaire. Ceci permet de calculer la valeur de la constante de vitesse k . On trouve $10.8 \cdot 10^{-2} \pm 0.2$: DENBIGH a précisément trouvé cette valeur, qui correspond également aux travaux classiques de WALKER et REICHERT.

Le temps d'atteinte de l'état stationnaire est aussi pratiquement celui de DENBIGH, environ 8 fois le temps de passage (le degré d'approximation est fonction du temps).

Il est remarquable que l'appareil de DENBIGH et le nôtre, de forme complètement différente, donnent le même résultat pour la même réaction. L'appareil de PIRET qui est aussi différent de l'un que de l'autre donne les résultats prévus d'après les mesures statiques pour une autre réaction. Ceci montre que le réacteur étagé est bien un appareil *extrapolable* pourvu que les conditions que nous avons énoncées soient respectées.

Les opérations expérimentales citées ici ont été en grande partie effectuées par Mr. DENYS VESCO à qui nous exprimons ici nos sincères remerciements.

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Etudes d'équilibres liquide-vapour 2

- (a) Système Benzène-Diméthylformamide sous un atmosphère absolu
- (b) Système Méthanol-Diméthylformamide sous un atmosphère absolu

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Summary—Experimental study of the liquid-vapour relationships in two binary systems, with quite different boiling points. Comparison with Gibbs-Duhem theoretical equation.

Two different experimental methods have been necessary to get reliable results whose validity is checked by various criteria.

No previous figures have been found in the literature for these binaries.

Résumé—Détermination expérimentale du diagramme d'équilibre liquide-vapeur des deux binaires :

- Benzène-Diméthylformamide
- Méthanol-Diméthylformamide

Les résultats sont comparés avec ceux déduits de l'équation théorique de Gibbs-Duhem.

L'intérêt de ce travail réside dans l'étude de deux systèmes à points d'ébullition éloignés par deux méthodes différentes et dans la comparaison entre différents critères de vérification.

Les deux binaires étudiés ici, n'ont fait l'objet, à notre connaissance, d'aucune publication.

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1. PURETE DES CONSTITUANTS

(a) Benzène

Le produit de départ est un benzène technique purifié par des procédés chimiques puis par rectification soignée.

Le processus de purification a été le suivant :

(a) lavage du produit technique par l'acide sulfurique concentré jusqu'à ce que l'acide ne soit plus coloré.

(b) lavage par une solution de carbonate de soude puis à l'eau pure.

(c) séchage par SO_4^2Na^2 anhydre.

(d) refroidissement de façon à ce que les environ de la quantité traitée soient solidifiés, le dernier quart étant rejeté. Cette opération est répétée trois fois ; on élimine ainsi les traces de toluène.

(e) nouveau séchage, puis rectification sur sodium dans une colonne à haut pouvoir séparateur.

On arrive de cette façon à un produit ayant un degré de pureté très élevé comme l'indique le tableau 1.

(b) Méthanol

Le méthanol est obtenu pur par rectification dans une colonne à haut pouvoir séparateur. Dans le Tableau 1, on compare les caractéristiques du produit utilisé avec celles données par littérature.

(c) Diméthylformamide

La diméthylformamide est obtenue à partir du formiate de méthyle et de la diméthylamine anhydre suivant la réaction :



Les deux constituants du mélange réactionnel (méthanol et diméthylformamide) sont séparés par distillation. La diméthylformamide est ensuite épurée par rectification sous un vide de 15 mm Hg. ce qui correspond à une température de passage de 48° .

Les constantes physiques des produits obtenus après les traitements d'épuration figurent dans le tableau 1.

Les indices de réfraction ont été déterminés au

A. DELZENNE : Etudes d'équilibres liquide-vapeur 2

Tableau 1

| | Benzène | | Méthanol | | Diméthylformamide | |
|---------------------------------|--------------|----------------|------------------|-----------------------|-------------------|---------------------|
| | Expérimental | Littérature | Expérimental | Littérature | Expérimental | Littérature |
| Indice de réfraction n_D^{20} | 1.5012 | 1.50142 [1] | 1.3312 à 14°5 | 1.33118 [1] à 14°5 | 1.4265 à 25° | 1.4269 [2] à 25° |
| Densité d_4^{20} | 0.8778 | 0.8794 [1] | 0.7951 | 0.7928 | 0.945 à 25° | 0.9445 [2] à 25° |

moyen du réfractomètre FERY-VAURABOURG donnant la 4ème décimale exacte.

Les densités ont été déterminées au moyen d'un pionomètre.

2. TENSIONS DE VAPEUR

Le Tableau 2 reproduit les valeurs des tensions de vapeur des constituants purs trouvés dans la littérature, tout au moins en ce qui concerne le benzène et le méthanol.

Par contre, nous n'avons trouvé dans la littérature que bien peu de données relatives à la diméthylformamide. Seuls sont mentionnées les points d'ébullition sous 758 mm Hg et 39 mm Hg [3] et il a été jugé préférable de déterminer

expérimentalement la courbe de tension de vapeur de la diméthylformamide.

On a utilisé pour cette détermination un ébulliomètre de Swietolawski, la partie supérieure du condenseur étant reliée d'une part à un manomètre à mercure précis, et d'autre part à une pompe à vide. Entre la pompe et l'ébulliomètre on a placé un réservoir de 10 litres servant de régulateur de pression. On introduit dans l'ébulliomètre, un mélange de composition déterminée et quand la pression désirée est atteinte, on note la température indiquée par un thermomètre de précision.

Les résultats sont rassemblés dans le Tableau 2 et représentés sur la Figure 1.

Tableau 2

| Pression en mm Hg | Benzène [4] | | | | | | | | | |
|-------------------|-------------------|-------|-------|-------|-------|-------|--------|-------|-------|-------|
| | 1 | 5 | 10 | 20 | 40 | 60 | 100 | 200 | 400 | 760 |
| Température en °C | -31.7 | -19.6 | -11.5 | -2.6 | +7.6 | +15.4 | +26.1 | +42.2 | +60.6 | +80.1 |
| Pression en mm Hg | Méthanol [4] | | | | | | | | | |
| | 1 | 5 | 10 | 20 | 40 | 60 | 100 | 200 | 400 | 760 |
| Température en °C | -44 | -25.3 | -16.2 | -6 | +5 | +12.1 | +21.2 | +34.8 | +49.9 | +64.7 |
| Pression en mm Hg | Diméthylformamide | | | | | | | | | |
| | 15 | 30 | 60 | 100 | 200 | 400 | 760 | | | |
| Température en °C | +48.2 | +63.5 | +78 | +90.6 | +10.5 | +130 | +153.4 | | | |

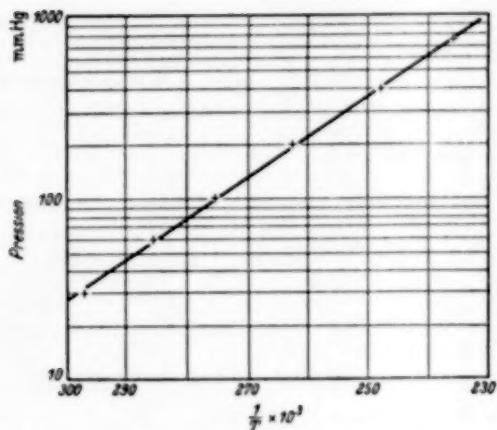


Fig. 1. Courbe de tension de vapeur de la diméthylformamide.

Pour l'interpolation nécessaire à tous les calculs, on a utilisé la formule connue :

$$\log P = A - \frac{B}{T}$$

qui se traduit par une droite sur un diagramme à ordonnées logarithmiques.

3. ANALYSE DES ECHANTILLONS

L'analyse des échantillons a été faite par réfractométrie, les courbes $n_D^{20} = f(x)$ ayant été déterminées au préalable pour les deux systèmes étudiés. Les valeurs correspondantes sont reportées sur le Tableau 3 et sur les Figures 2 et 3.

Tableau 3

| Système Benzène-Diméthylformamide | | Système Méthanol-Diméthylformamide | |
|-----------------------------------|---------------------------------|------------------------------------|---------------------------------|
| Titre moléculaire en benzène | Indice de réfraction n_D^{20} | Titre moléculaire en méthanol | Indice de réfraction n_D^{20} |
| 0 | 1.4285 | 0 | 1.4285 |
| 0.100 | 1.4380 | 0.145 | 1.4227 |
| 0.230 | 1.4482 | 0.250 | 1.4164 |
| 0.350 | 1.4580 | 0.355 | 1.4100 |
| 0.530 | 1.4710 | 0.500 | 1.3981 |
| 0.710 | 1.4835 | 0.650 | 1.3822 |
| 0.850 | 0.4922 | 0.755 | 1.3700 |
| 1 | 1.5012 | 0.900 | 1.3471 |
| | | 1 | 1.3292 |

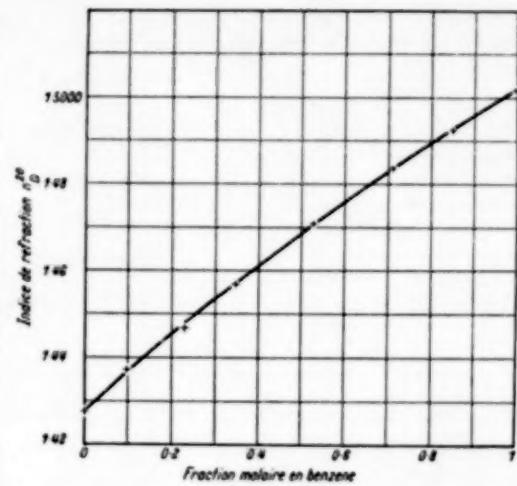


Fig. 2. Système benzene-diméthylformamide. Courbe $n_D^{20} = f(x)$.

4. DESCRIPTION DES METHODES EXPERIMENTALES

(a) Méthode par condensation et recirculation du condensat

La détermination des équilibres liquide-vapeur par cette méthode a été faite en utilisant l'appareil d'OTHMER [5].

Une charge totale de 400 cc. est utilisée pour chaque essai, le régime est établi au bout de deux

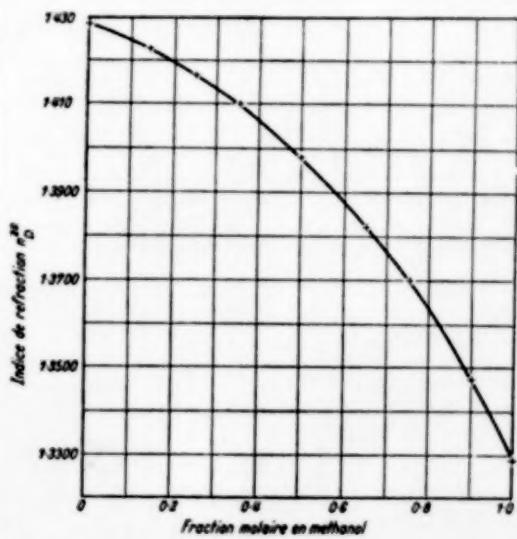


Fig. 3. Système Méthanol-Diméthylformamide. Courbe $n_D^{20} = f(x)$.

A, B. Saturateurs.
 C. Chambre d'équilibre.
 R. Vaporisateur.
 D. Prise d'échantillon de la phase liquide.
 E. Prise d'échantillon de la phase vapeur.
 F. Gaine thermométrique.
 G. Bain thermostatique.
 H. Enroulement chauffant.

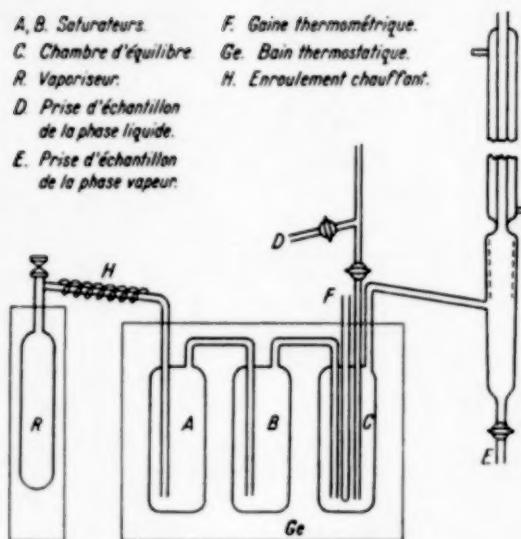


Fig. 4. Appareil pour la détermination des équilibres Liquide. Vapeur par la méthode dynamique.

heures d'ébullition environ. On prélève alors un échantillon de la phase vapeur condensée et un échantillon de la phase liquide que l'on soumet immédiatement à l'analyse.

La température est enregistrée au moyen d'un thermomètre de précision à $\pm 0.1^\circ\text{C}$.

(b) Méthode dynamique

Comme on le verra plus loin, l'emploi de l'appareil d'OTHMER ayant donné lieu à des mécomptes pour l'étude de l'un des systèmes, nous avons été amenés à utiliser dans ce cas la méthode dynamique dont nous rappelons brièvement le principe.

On introduit dans une chambre d'équilibre portée à une certaine température et contenant le mélange à étudier, le constituant le plus volatil sous forme gazeuse.

L'appareillage est représenté sur la Fig. 4. Il comprend deux saturateurs *A* et *B* et une chambre d'équilibre *C*; ces trois récipients, reliés entre eux, sont plongés complètement dans un bain d'eau ou d'huile suivant la température que l'on veut atteindre. La chambre d'équilibre est munie d'une tubulure plongeante permettant de prélever un échantillon de la phase liquide, d'une deuxième tubulure permettant l'évacuation des vapeurs et

d'une gaine thermométrique pour l'enregistrement de la température.

Le constituant volatil vaporisé dans le récipient *R* est envoyé dans les saturateurs *A* et *B* et dans la chambre d'équilibre *C*, où les vapeurs barbotent dans le binaire à étudier. La phase vapeur est condensée à la sortie de la chambre d'équilibre et recueillie dans un récepteur. On maintient la température constante dans le bain et après deux heures de barbotage, on prélève un échantillon de la phase liquide et un échantillon de la phase vapeur condensée.

La température est lue au moyen d'un thermomètre de précision ($\pm 0.1^\circ\text{C}$).

5. CALCUL DES COEFFICIENTS D'ACTIVITÉ – VERIFICATION DES RÉSULTATS EXPERIMENTAUX

(a) Calcul des coefficients d'activité

Il est connu que la valeur des données expérimentales est vérifiée dans les meilleures conditions par le calcul des coefficients d'activité. Ces coefficients s'obtiennent au moyen des relations suivantes :

$$\text{et} \quad \gamma_1 = \frac{P y_1}{P_1^* x_1} \quad (1a)$$

$$\gamma_2 = \frac{P y_2}{P_2^* x_1} \quad (1b)$$

où γ_1 et γ_2 = coefficients d'activité

P = pression d'expérience

x = titre moléculaire dans le liquide

y = titre moléculaire dans la vapeur

et ces calculs permettent de tracer les courbes

$$\gamma_1 = f(x_1) \quad \text{et} \quad \gamma_2 = f(x_1)$$

(b) Vérification

(a) L'exactitude de ces résultats est vérifiée en premier lieu au moyen des équations de VAN LAAR déduites de la relation générale de Gibbs-Duhem.

Les courbes résultant de l'application de ces équations sont ensuite tracées en pointillés pour comparaison avec les courbes déduites directement des données expérimentales (en trait plein).

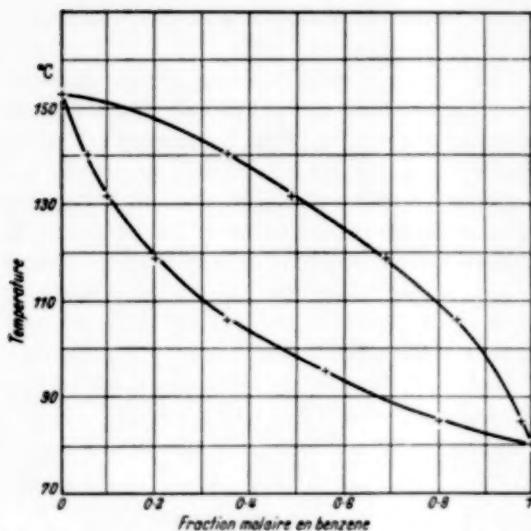


Fig. 5. Système benzene-dimethylformamide. Courbes d'ébullition et de rosée.

(b) On vérifie ensuite si les pentes des tangentes des courbes $\log \gamma = f(x_1)$ répondent à l'équation.

$$\frac{d \log \gamma_1}{dx_1} = \left(\frac{1-x}{x} \right) \left(\frac{d \log \gamma_2}{dx_2} \right) \quad (4)$$

On choisit pour cela un point sur la courbe $\log \gamma_1 = f(x_1)$ ayant pour abscisse une valeur déterminée x_1 et on mesure la pente de la tangente en ce point. On mesure d'autre part, la pente de la tangente à la courbe $\log \gamma_2 = f(x_1)$ en un point situé sur la courbe $\log \gamma_2 = f(x_1)$ et ayant pour abscisse la même valeur x_1 . Le rapport de ces pentes doit être égal à $-\left(\frac{1-x}{x}\right)$

(c) On vérifie enfin que les courbes $\log \frac{\gamma_1}{\gamma_2} = f(x_1)$ satisfont à la relation :

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} = 0 \quad (5)$$

Cette relation s'établit à partir de l'excès d'énergie libre par molécule de mélange, grandeur qui est égale à :

$$\Delta F = R T \cdot \Sigma [x_i \ln \gamma_i] \quad (6)$$

En d'autres termes, on vérifie donc l'égalité des

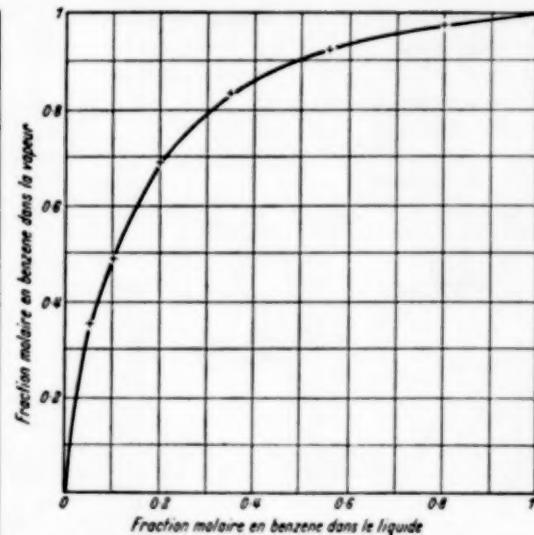


Fig. 6. Système benzene-dimethylformamide. Courbe $y = f(x)$.

aires comprises entre la courbe $\log \frac{\gamma_1}{\gamma_2} = f(x_1)$, la droite horizontale d'ordonnée $\log \frac{\gamma_1}{\gamma_2} = 0$ et les droites verticales d'abscisses $x_1 = 0$ et $x_1 = 1$. Ces aires doivent être égales, à quelques unités près, de leur valeur.

Tableau 4
Données expérimentales de l'équilibre liquide-vapeur du système Benzène-Diméthylformamide

| Temp. en °C | x_1 | y_1 | γ_1 | γ_2 | $\log \gamma_1$ | $\log \gamma_2$ |
|-------------|-------|-------|------------|------------|-----------------|-----------------|
| 140 | 0.055 | 0.355 | 1.380 | 0.935 | 0.140 | -0.029 |
| 131.5 | 0.100 | 0.490 | 1.260 | 1.005 | 0.110 | 0.002 |
| 119 | 0.200 | 0.690 | 1.160 | 1.030 | 0.075 | 0.018 |
| 106 | 0.350 | 0.835 | 1.110 | 1.060 | 0.050 | 0.025 |
| 95.2 | 0.560 | 0.925 | 1.062 | 1.120 | 0.026 | 0.052 |
| 91 | 0.655 | 0.945 | 1.045 | 1.185 | 0.019 | 0.074 |
| 85 | 0.800 | 0.975 | 1.029 | 1.230 | 0.012 | 0.090 |

6. RESULTATS EXPERIMENTAUX

(a) Système Benzène-Diméthylformamide

La détermination de l'équilibre liquide-vapeur de ce système a été faite au moyen de l'appareil d'OTHMER.

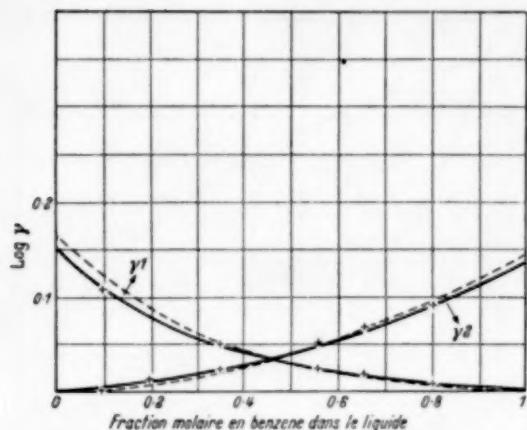


Fig. 7. Système benzene-dimethylformamide. Courbes $\log \gamma = f(x_1)$.

Les résultats expérimentaux sont rassemblés dans le tableau 4 et représentés sur les Figures 5 et 6.

La Figure 5, concerne le faisceau d'ébullition et de rosée ; la Figure 6 traduit la relation $y = f(x)$ indépendamment de la température.

Les coefficients d'activité calculés au moyen des équations (1a) et (1b) sont reportés sur la Figure 7.

Contrôle et vérification

Les valeurs de A et B calculées à partir de $x_1 = 0.560$ sont les suivantes :

$$\begin{aligned} A &= 0.160 \\ B &= 0.135 \end{aligned}$$

Les courbes résultant de l'application des équations de VAN LAAR, à partir de ces valeurs A et B , ont été tracées en pointillés sur la Figure 7. L'accord entre ces dernières et les courbes expérimentales (en trait plein) est fort satisfaisant si l'on tient compte, d'une part que les équations de VAN LAAR sont établies pour une série de mesures isothermes et, d'autre part, que l'écart entre les points d'ébullition est assez considérable. Une telle concordance a d'ailleurs déjà été observée par d'autres auteurs [6].

La relation 4 est, elle aussi, sensiblement vérifiée comme l'indique le tableau 5, suivant, tableau dans lequel M_1 représente le premier membre de la relation, M_2 le deuxième membre.

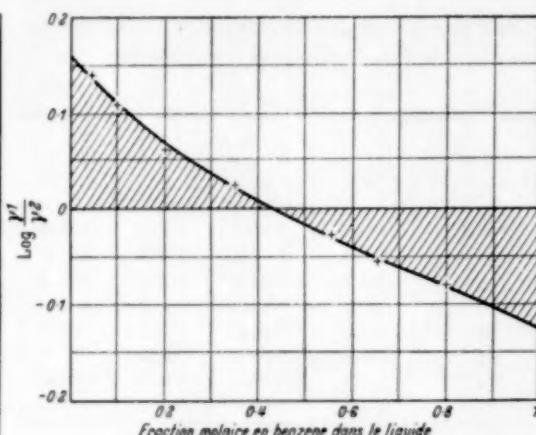


Fig. 8. Système benzene-dimethylformamide. Courbe

$$\log \frac{y_1}{y_2} = f(x_1).$$

Tableau 5

| x_1 | M_1 | M_2 |
|-------|-------|-------|
| 0.100 | 0.491 | 0.500 |
| 0.200 | 0.289 | 0.267 |
| 0.350 | 0.150 | 0.165 |
| 0.560 | 0.115 | 0.125 |
| 0.800 | 0.052 | 0.050 |

Enfin on a tracé sur la Figure 8, la courbe $\log \frac{y_1}{y_2} = f(x_1)$ à partir des données expérimentales. L'égalité des aires hachurées, réalisées à 4-3 % près, montre que la courbe satisfait à la relation 9.

(b) Système Méthanol-Diméthylformamide

Les premières séries d'expériences ont été effectuées avec un appareil d'OTHMER semblable au précédent ; mais on a obtenu des résultats très dispersés - (Tableau 6, Figure 9).

Les irrégularités constatées sont dues au fait que l'ébullition, au lieu d'être régulière, se faisait par à coups avec formation de très grosses bulles de vapeur qui perturbaient l'établissement de l'équilibre.

Différents remèdes, tels que l'adjonction de corps poreux ou de tubes de verre, le chauffage

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interne par résistance électrique, ont été essayés sans obtenir l'ébullition régulière désirée.

Tableau 6

| Température en °C | x_1 | y_1 | γ_1 | γ_2 |
|-------------------|-------|-------|------------|------------|
| 143.2 | 0.035 | 0.480 | 1.220 | 0.740 |
| 136 | 0.070 | 0.720 | 1.085 | 0.520 |
| 123.7 | 0.150 | 0.810 | 0.781 | 0.595 |
| 110.8 | 0.250 | 0.840 | 0.710 | 0.930 |
| 95.8 | 0.405 | 0.932 | 0.765 | 0.870 |
| 81 | 0.595 | 0.980 | 0.895 | 0.758 |
| 75 | 0.700 | 0.990 | 0.935 | 0.650 |
| 70.5 | 0.820 | 0.996 | 0.952 | 0.545 |

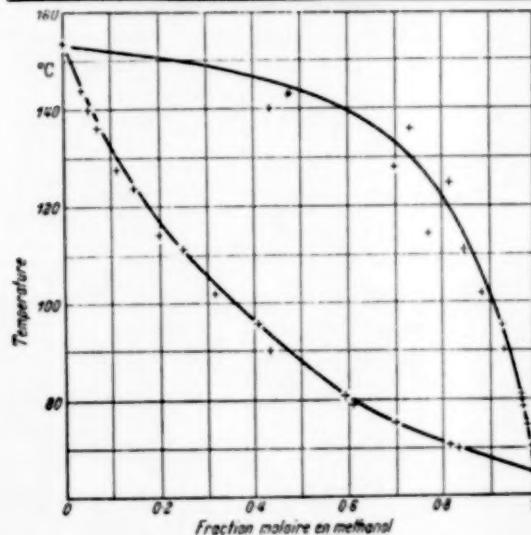


Fig. 9. Système méthanol-diméthylformamide. Courbe d'ébullition et de rosée (Méthode par recirculation-Appareil d'OTTHMER).

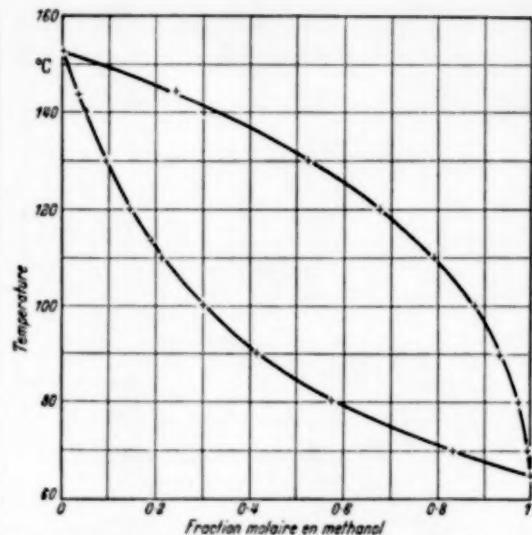


Fig. 10. Système méthanol diméthylformamide. Courbes d'ébullition et de rosée. (Méthode dynamique).

D'après ce tableau il est visible que les valeurs de γ ne sont pas acceptables. Si abstraction faite de la dispersion des points expérimentaux, on trace une courbe moyenne pour γ_1 et pour γ_2 , ces courbes passeront dans l'un et l'autre cas par un minimum. Ce qui n'est pas justifié au point de vue thermodynamique.

Devant cet insuccès, on a donc décidé de faire l'étude de l'équilibre liquide-vapeur de ce système par la méthode dynamique qui a été décrite plus haut.

Les résultats expérimentaux ont été rassemblés dans le tableau 7, et les courbes qui en sont

Tableau 7
Données expérimentales de l'équilibre Liquide-Vapeur du système Méthanol-Diméthylformamide

| Température en °C | x_1 | y_1 | γ_1 | γ_2 | $\log \gamma_1$ | $\log \gamma_2$ |
|-------------------|-------|--------|------------|------------|-----------------|-----------------|
| 140 | 0.045 | 0.300 | 0.626 | 1 | -0.203 | 0 |
| 130 | 0.095 | 0.525 | 0.673 | 0.985 | -0.172 | -0.007 |
| 120 | 0.145 | 0.675 | 0.756 | 0.982 | -0.121 | -0.008 |
| 110 | 0.210 | 0.790 | 0.795 | 0.970 | -0.100 | -0.014 |
| 100 | 0.300 | 0.875 | 0.850 | 0.955 | -0.072 | -0.020 |
| 90 | 0.415 | 0.930 | 0.910 | 0.928 | -0.041 | -0.033 |
| 80 | 0.575 | 0.968 | 0.956 | 0.880 | -0.019 | -0.056 |
| 70 | 0.830 | 0.9924 | 0.960 | 0.790 | -0.018 | -0.103 |

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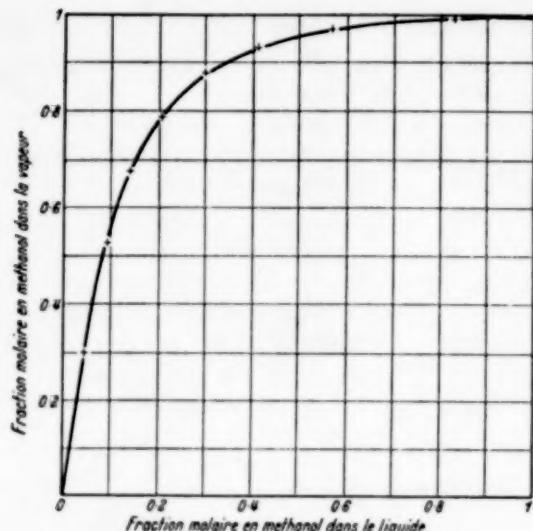


Fig. 11. Système méthanol-diméthylformamide. Courbe d'équilibre liquide-vapeur.

Tableau 8

| x_1 | M_1 | M_2 |
|-------|-------|-------|
| 0.145 | 0.544 | 0.537 |
| 0.210 | 0.409 | 0.376 |
| 0.300 | 0.251 | 0.230 |
| 0.415 | 0.174 | 0.169 |
| 0.575 | 0.095 | 0.115 |

faisant entre les courbes expérimentales (en trait plein) et les courbes déduites des équations de VAN LAAR (en pointillés, à part de ces valeurs de A et B .

D'autre part, la relation qui existe entre les pentes des tangentes aux courbes $\log \gamma_1 = f(x_1)$ et $\log \gamma_2 = f(x_1)$ est approximativement vérifiée comme l'indique le tableau 8.

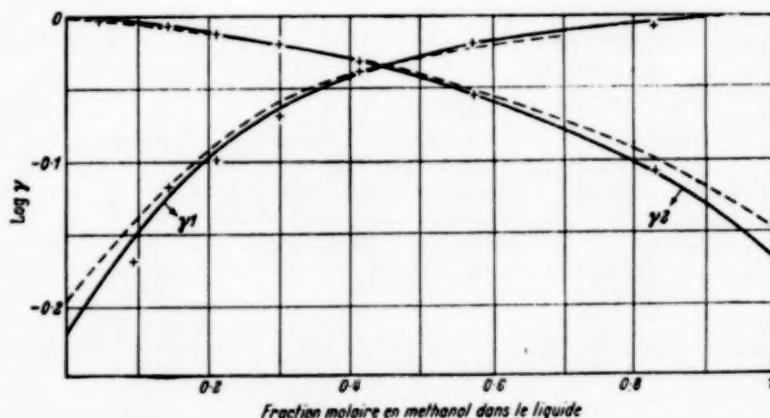


Fig. 12. Système méthanol-diméthylformamide. Courbes $\log \gamma = f(x)$.

déduites, tracées sur les Figures 10 et 11. Les coefficients d'activité, calculés comme précédemment, sont reportés sur la Figure 12.

Vérification et contrôle

Les valeurs de A et B , calculées à partir de $x_1 = 0.415$, sont les suivantes:

$$A = -0.196$$

$$B = -0.125$$

La Figure 12 montre qu'il y a un accord satis-

En dernier lieu, on a tracé sur la Figure 18, la courbe $\log \frac{\gamma_1}{\gamma^2} = f(x_1)$. L'égalité des aires hachurées est vérifiée à 3% près. Les données expérimentales satisfont donc, de façon acceptable à la relation :

$$\int_0^1 \log \frac{\gamma_1}{\gamma^2} = 0$$

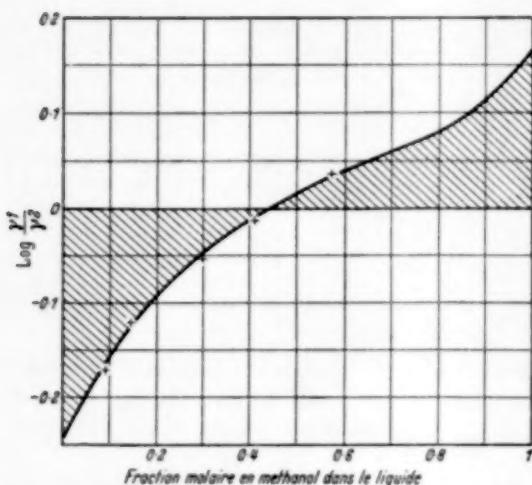


Fig. 13. Système méthanol-diméthylformamide. Courbe

$$\log \frac{y_1}{y_2} = f(x_1).$$

CONCLUSIONS

Les systèmes binaires Benzène-Diméthylformamide et Méthanol-Diméthylformamide ne sont

pas des systèmes idéaux.

Si l'étude du premier système est réalisable par la méthode de recirculation au moyen d'un appareil d'OTHMER courant, celle du second s'est révélée irréalisable dans ces conditions. La méthode dynamique a permis de surmonter cette difficulté.

Les résultats expérimentaux sur l'équilibre liquide-vapeur de ces deux systèmes ont été soumis à différents critères dérivés de la thermodynamique des solutions. Les courbes expérimentales obtenues montrent vis-à-vis de celles déduites de ces critères, un accord satisfaisant.

NOMENCLATURE

x = titre moléculaire d'un constituant dans le liquide

y = titre moléculaire d'un constituant dans la vapeur

P = pression d'expérience

p° = tension de vapeur d'un constituant à une température déterminée

γ = coefficient d'activité

A et B = constantes des équations de VAN LAAR

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Book reviews

R. C. L. BOSWORTH : Heat Transfer Phenomena. Associated General Publications, Pty. Ltd., Sydney. John Wiley & Sons Inc., New York. Pergamon Press Ltd., London, 1952. £3. 10s. (Australian) or \$6.00 or 42s.

THIS monograph forms an extension and addition to the opening paper read at a conference on Heat Transfer at Sydney in 1948. As the author says in his preface, the book comprises "essentially a review of recent developments in Heat Transfer and is concerned with: the conduction of heat in gases, radiative transfer, conduction in solids and liquids, forced and natural convection, heat flow with simultaneous phase change and the use of electrical and other model methods." Indeed, the book is not meant as a handbook for those concerned with thermo-technical calculations, but merely provides an exposition of the present fundamental insight into the various fields of heat transfer as well as of the difficulties still to be overcome. In this respect the book is a very welcome addition to the well-known handbooks and enables the reader, with little effort, to become familiar with this more fundamental background of heat transfer problems.

Owing to the size of the book, every problem is dealt with rather summarily. However, thanks to the lucidity of the author, who consistently treats all forms of heat transfer from the point of view of "carrier-mean free path," the work has become a most attractive exposition which reads like a novel for those who are at all acquainted with heat transfer problems. The numerous references at the end of every chapter present sufficient points of departure for a more profound study of the various subjects.

However, the book shows that the author - who has already made several contributions to the literature in this field - evinces a partiality for some of the problems treated. This accounts for the fact that the book suffers from a certain lack of balance as regards the attention given to the various subjects.

For example, in addition to the brief discussion of dimensional analysis in the chapters on natural and forced convection, 15 pages of the last chapter are devoted to a rather fruitless treatment of thermodynamical similarity, whereas the important subject of analogy between heat and mass transfer is disposed of in slightly over 2 pages. "The use of the equivalent electrical circuit" receives 22 pages, but no attention is given to the recent development in the field of heat transfer at very high gas velocities.

Apart from this criticism in comparatively minor points, the author may be said to have succeeded in treating the comprehensive subject of heat transfer in a concise but nevertheless extremely lucid way. In consequence the book is particularly suited for teaching purposes, although its rather high price prevents its extensive use as a text book.

Finally, it would be commendable in a subsequent edition to expend as much care on the figures as has been bestowed on the printed text, and to consistently use the kg.cm.sec. Joule system instead of expressing the various quantities in arbitrarily selected units (radiative constant σ in erg. cm⁻² sec⁻¹ k⁻⁴ and B.T.U.'s ft⁻² hr⁻¹ °R⁻⁴, radiancy of gases E in kgcal m⁻² hr⁻¹, thermal conductivity k in cal. cm⁻¹, sec⁻¹, °C⁻¹, heat transfer coefficient h in B.T.U.'s ft⁻² hr⁻¹ °F⁻¹). This alteration would be welcomed, especially in this book which forms a link between the technical and the fundamental science.

C. v. HEERDEN.

E. A. GUGGENHEIM : Mixtures. Oxford University Press 1952, 42s.

L'auteur dont le traité "Statistical Thermodynamics," rédigé en collaboration avec FOWLER, est un classique dans tous les pays et dont le plus récent *Thermodynamics* est un exemple de précision, présente avec clarté et simplicité sa théorie des solutions strictement régulières. Après un rappel de thermodynamique classique et une introduction aux méthodes de la mécanique statistique, il expose la théorie des solutions liquides "s. régulières" (première approximation et approximations supérieures) qu'il met en parallèle avec la méthode quasichimique de BETHE et celle de KIRKWOOD. Il compare ensuite les résultats théoriques et expérimentaux.

De l'étude des solutions liquides diluées, l'auteur passe à celle des imperfections dans les cristaux. Il étudie ensuite les réseaux cristallins surimposés (point λ). Les mêmes approximations que précédemment sont utilisées. L'auteur passe ensuite à la mécanique statistique des mélanges gazeux parfaits et réels en liaison avec la théorie des "états correspondants." Un chapitre est consacré à la thermodynamique et à la statistique des solutions superficielles, nouvelle application de la théorie des solutions "s. régulières."

L'étude des solutions athermes et non athermes (molécules de dimensions différentes) et des solutions de macromolécules complète cet exposé des théories simples particulièrement fécondes et dont les résultats peuvent souvent être raisonnablement confrontés avec les expériences.

Bien entendu, dès l'introduction, l'auteur insiste sur le fait que ces modèles ne peuvent prétendre représenter que les solutions les plus simples. Mais ceci permet néanmoins de traiter quantitativement des problèmes qui sont d'ailleurs suffisamment compliqués pour être intéressants.

A. POTIER

Book reviews

J. H. DE BOER : **The Dynamical Character of Absorption.** 1953, O.U.P., 30/-, 239 p., XV. p.p., 45 figs.

To his well-known work on the emission and absorption of electrons DR. DE BOER has added this lively book on the physical adsorption of molecules. The importance of a mechanical picture of the kinetic processes of physical adsorption and of the conditions in layers of molecules is strongly emphasized. Because they have been the subject of an article by the author (in *Advances in Catalysis* Volume II) energy relationships do not receive prominence.

The introduction of the book outlines the kinetic approach: the terms in the fundamental equation
Collision frequency \times Lifetime on surface = Number of molecules with surface

are dealt with individually in the first few chapters and it is here that the pictorial aspect is stressed. Perhaps overstressed; for a discussion of energy and entropy of adsorption we have to be content with brief accounts in later chapters.

The latter and larger part of the book considers the properties of the adsorbed layer in terms of a 2-dimensional gas. Beginning with ideal behaviour this account goes on to introduce constants (b_2 and a_2) corresponding to those of the van der Waals equation for the 3-dimensional gas. These constants form the basis of a treatment of condensation and critical phenomena in two dimensions which is extended to adsorption equilibrium - monolayer, multilayer and finally condensation. The last chapter of the book is virtually an appendix on capillary effects.

The opening chapters have an attractive vigour and clarity which will appeal to most readers. The clarity of later sections might have been increased further if chapters had been here added on the energetics of adsorption and the thermodynamic properties of mobile adsorbed layers. The use of van de Waals equation which has the advantage of familiarity could have been supplemented by a clear summary of relations between it and its constants with those of a virial expansion.

Despite this unevenness the book is a unique and stimulating account of physical adsorption, and will be of great value to all who deal with these problems.

P. GRAY.

F. WILD : **Estimation of Organic Compounds**, 239 p.p. Cambridge University Press, 1953, 25s. net.

The author describes different methods for the estimation of groups in organic compounds and of certain compounds, e.g. the olefines, hydroxyl groups containing compounds, mercaptans, carbonyl compounds, amines, nitro, cyano and nitroso compounds.

The reviewer thinks that DR. WILD has been successful in the choice of the compounds in question, many of these

being of importance for the organic chemical industry. The description of the methods is thorough.

In determining the hydrogen value of olefines it is useful to investigate the hydrogenated product, in order to check if it is really the expected product. It is known that for the examination of oils and fats the thiocyanogen number is a "distinctive number" having a certain significance, only when all the conditions during the determination are fixed within very definite limits.

Stress could be laid still more on the necessity for the application of the hydrogen values. The author does this for gaseous olefines; he says: "catalytic hydrogenation is the only rapid method, giving a reliable indication of the degree of unsaturation."

The halogen numbers are often not correct, the halogen addition generally depends on an equilibrium.

VAN DER STEUR showed that the equilibrium constants are dependant not only on the temperature (they rise with decreasing temperature), but also on the nature and the position of the double bond.

This book is very valuable, it can be recommended to the research and analytical laboratories, which have to investigate or to synthesize the compounds discussed in the book. It has an excellent subject and author index.

H. I. WATERMAN

Food Investigation, 1952. Published by Dept. of Scient. and Industr. Res. H.M. Stationery Office, 1953. 56 pp. Price 2s. (U.S.A. : 50 cents).

This report covers the wide range of activities of the Food Investigation Board, and gives an interesting general picture of the problems which are being tackled. A large proportion of the work is concerned with the development of improved methods of storage, particularly of meat, fish and fruit and vegetables, so as to prevent deterioration of quality. An interesting point is that, whereas some fish is found to have deteriorated after a month in cold store, its quality improves again after a further two months' storage.

Chemical Engineers will be interested in the work on heat transfer at low temperatures. Research is being carried out in an air blast tunnel freezer, on the effect of air temperature, velocity, turbulence and relative humidity on the rate of heat transfer to slabs of fish; temperatures are measured by means of thermocouples in the solid and in the air stream. Freeze concentration of beer and evaporation at low temperatures are being studied in co-operation with the brewers' organizations. Improved methods of drying fruit and vegetables and the dehydrating of meat are being developed. An incidental problem is the tin plating of aluminium for use in canning, in order to prevent corrosion and to enable it to be soldered.

J. F. RICHARDSON.

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A. G. GAYDON and H. G. WOLFHARD : **Flames : Their structure and radiation.** Chapman and Hall, 1953. 340 pages. Price 55s.

A great deal of work has been done on flames since BONE and TOWNSEND's *Flame and Combustion in Gases* was published in 1927, and numerous texts have appeared since then. Outstanding among those available in English today are the translation of JOST's excellent *Explosion and Combustion Processes in Gases* (1935) and LEWIS and VON ELBE's *Combustion Flames and Explosions in Gases* (1951). These two texts have become standard works for students of flame. To them has now been added *Flames* by Dr. GAYDON and Dr. WOLFHARD. The authors' close connection with nearly every aspect of the subject they discuss is obvious. It is a valuable contribution.

The early chapters (I, II) are concerned with flames in premixed gases. A general descriptive account is given of their properties ; more general material may also be found in a later chapter (XIV). A detailed account (III) of flow patterns in flames and of the shapes of flame fronts follows : the influence of sound on flame shape and propagation, and the acoustic effects of flames are not considered until a later chapter (VII). Experimental methods of measuring flame speed are listed and their reliability discussed ; this section (IV) receives particular emphasis. The mechanism of flame propagation is then considered (V) and a discussion of turbulent flames is included ; chemical kinetics of combustion processes are not discussed though the mechanism of carbon formation is considered in some detail (VIII). Both thermal and diffusion theories of steady flame propagation are considered and various explosions are quoted relating burning velocity to the other parameters typical of the flame and the chemical reactions occurring in it. The authors consider that problems of spontaneous ignition, critical ignition energy and flame stability, which might have found a place here, and which have been dealt with at length by JOST, and by LEWIS and VON ELBE, to be beyond the scope of this book. They also deliberately avoid purely mathematical discussion ; but a more critical comparison and assessment of the basic assumptions of different theories would have been a valuable contribution to this section. Diffusion flames are described in chapter VI. The results obtained by the authors by the spectroscopic examination of flat diffusion flames are described, and diffusion and pre-mixed flames are contrasted. Turbulent diffusion flames, furnace flames, flames of droplets, of fuels on wicks and of the candle are considered briefly. Solid particle combustion is mentioned later (XIV). A chapter (IX) follows on radiation processes in flames. This section centres on the problems of dis-equilibrium both of energy distribution and of chemical reaction and forms a valuable introduction to the discussion of flame temperature (X, XI, XII). The validity of the concept of temperature, and the theoretical and practical limitations of the various methods of measurement are discussed with clarity. This

valuable section ends with the systematic calculation of flame temperatures ; typical results are given for a variety of flames. Ionization in flames (XIII), a process notoriously out of equilibrium, follows aptly the radiation and temperature sections and ends the formal topic of the book. Chapter XIV "Some unusual flames" which follows, contains a miscellany of recent information ; various unresolved problems are summarized in Chapter XV.

Some lack of logical development may be felt in the authors' exposition. But no one exclusive arrangement of subject matter exists and its lively treatment here affords ample compensation. It is an excellent book.

PETER GRAY.

CARL MITTAG : **Die Hartzerkleinerung** (The Milling of Hard Materials) Springer-Verlag, Berlin/Göttingen/Heidelberg, 1953. vi + 342 pages, 190 illustrations. DM 40.50.

CARL MITTAG is the Grand Old Man of the practice of milling hard materials in Germany ; for more than 50 years he has worked in this field, which has expanded so rapidly in the last decades that a comprehensive survey would be a monumental task. MITTAG therefore selects his material be it of use to students in technical colleges and mining schools, to constructional and chemical engineers, and to industrial technologists and scientists, who may wish to learn the principles of milling hard materials, to choose the right mill for specific jobs or to improve upon existing types of mill.

The book is arranged in three parts. The first, after a short historical introduction, describes 27 types of crushing and milling machines. The second deals with the fundamental physics of the milling operation and the third describes ancillary equipment and experience in milling a number of important materials.

The first part, amounting to half the book, is most attractively arranged in a consistent pattern for each type of mill : an introduction, a description of the plant and its field of application. Of the 190 illustrations, all apparently drawn specially for the book, 129 are in the first part. Most of them are sections and show very well how the mills work, an advantage to readers with little or no German ; however, only the outside of the Hardinge mill is drawn, possibly because the author says on p. 150 that the principle of its working is unsound ; the reader will want to know why. Apart from a few apparent prejudices, this part of the book should indeed be useful to the classes of people to whom it is offered. By the use of numerous formulae, tables and graphs, it is possible, for many of the more important minerals of commerce, to determine the size of mill for a given output and grit.

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The theoretical part deals with some aspects of the fundamentals of comminution and gives some practical hints MITTAG has found useful. Chiefly following the work of VON RITTINGEN and KICK, and of SMEKAL and ANSLEM, MITTAG gives a useful summary of the relationship between the work done to produce new surface area in milling; the 'efficiency' of a mill can be judged by his calculations of this relationship, expressed throughout as so many g cm/cm².

For the measurement of particle size only ANDREASEN's pipette is mentioned, and the pages on micromeritics are curiously old-fashioned. The reason for this can be seen by referring to the list of references at the end of the book: 21 are pre-1928, 55 are 1928-37, and only 14 are post-1937 (up to 1949). None of the 19 English and U.S. papers referred to is after 1936, and 6 out of the 19 have spelling errors, including STOCK's law (also in the text) and A. F. TAGGERT.

Both in parts one and two a lot of information is given on the right speed and load of ball mills, but COGHILL and DE VANEY's and others' useful formulae for calculating the right size of balls is not given, much less OLEVSKY's more recent formula (1948).

Part two is concluded with a section on future developments in milling plant techniques based on explosion, the 'puffed wheat' and vibration principles, but some-

thing might have been said of 'micronising,' fluid energy mills and ultrasonic comminution.

The third part is intended to help the reader to find 'the right machine for the right job,' and has a valuable section on ancillary plant such as feeding and classifying plant, including sieving machines, wind-sifters, and dust separators. Wet classifying is illustrated by only one type of plant, but the other types of plant are as well illustrated and described as in part one.

The choice of plant for a given raw material is illustrated by descriptions of typical processes for the comminution of iron, copper, lead-zinc, tungsten, and tin ores; of coal, though not a hard material; of carbonate rocks, feldspar and quartzite; of cement slags, etc.; of calcium carbide and cyanamide; of phosphates and of carbon for making electrodes.

CARL MITTAG does not deal very much with the problems of extremely fine grinding, possibly because this is usually considered as a separate technical category in Germany (*Feinstzermahlung*); but few men can have had so much experience in the classical methods of milling in the heavy chemical industry, and his descriptions of the different sorts of mill will continue to be useful for many years because the older types, yes even millstones, will be with us for centuries.

R. H. S. ROBERTSON.

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